CATALYTIC PROPERTY OF FIBER MEDIA SUPPORTED PALLADIUM CONTAINING ALLOY NANOPARTICLES AND ELECTROSPUN CERAMIC FIBERS BIODURABILITY STUDY

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ABSTRACT

The nanoscale of the supporting fibers may provide enhancements such as restricting the migration of metal catalyst particles. In this work, palladium nanoparticle doped alumina fibers were electrospun into template submicron fibers. These fibers were calcined at temperatures between 650°C and 1150°C to vary the crystal structures of the calcined fibers with the Pd particle size. Higher calcination temperatures led to higher reaction temperatures from 250 to about 450°C for total conversion, indicating the effective reactivity of the fiber-supported catalysts decreased with increase in calcination temperature.

Pd-Au alloy nanoparticle doped titania fibers were also fabricated using an electrospinning method and assembled into a fibrous porous medium structure by a vacuum molding process. In reactor tests, the fiber media with Pd-Au alloy nanoparticle catalyst had greater reactivity in conversion of NO and CO gases than that of fiber media with Pd monometallic catalyst alone, attributed to a lower activation energy of the Pd-Au catalyst particles. In carbon monoxide oxidation reaction tests, the results showed that the performance was optimal for a catalyst of composition Pd$_2$Au$_1$ molar ratio that was active at 125°C, which had higher dispersion of active components and better catalytic performance compared to monometallic particle Au/TiO$_2$ and Pd/TiO$_2$ fiber media. Moreover, the improved
reaction activity of Pd$_2$Au$_1$/TiO$_2$ fiber medium was attributed to a decreased in the activation energy.

Further experiments were conducted using the electrospun ceramic fibers biodurability study. The properties of nano-sized fiber structures have attracted the attention of recent research on ceramic nanostructures as nonwoven media for applications in hazardous chemical and high temperature environments. However, health and safety concerns of micro and nano scale ceramic materials have not been fully investigated. Little is known about the physicochemical effects of the properties of small alumina fibers, including fiber sizes, surface morphologies, crystalline, phases, and surface areas with respect to submicron sized alumina fibers formed by calcination of electrospun polymeric fibers.

Therefore, in this work, sub-micron sized alumina fibers were fabricated by electrospinning and calcination of a polymer template fiber. In the calcination step, different controlled temperature heating cycles were conducted to obtain fibers of different crystalline structures. Their biodurabilities were evaluated in two types of artificial lung fluids (i.e., mimicking the airway and alveolar macrophages). Though the variation in the soak temperature, their dissolution half times were not significantly affected. The solubility half-times of the alumina fibers were shortest for fibers calcined at the fastest temperature ramp rate (though soak temperature did not have an effect).
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CHAPTER I

INTRODUCTION

1.1 Background and overview of work

Sub-micron and nanoscale (1 – 100 nm) diameter alumina fibers are of interest for a number of potential applications such as catalyst support structures, reaction substrates, filtration, and sensors [1-5]. The small diameters of the fibers, and the small dimensions of nanomaterials in general, enhance material properties through high surface areas per unit mass and enhance transport properties through slip and molecular flow effects [6]. The enhanced properties make these materials attractive to industries for development of new advanced fiber materials. Sub-micron and nanoscale diameter fibers are working their way into the fabrication processes of common materials such as filter media for air filtration [7].

When fuel is burned in air at high temperatures, nitrogen oxides (NOx) mainly containing NO and NO₂ are formed. The primary sources of NOx are automobiles, electric utilities, and other industrial, commercial, and residential sources [8]. When NO and NO₂ react with hydrocarbons in the presence of sunlight, they contribute to the formation of smog, ground-level ozone, acid rain, and human health issues. Industries are compelled by regulatory agency regulations to eliminate these potentially harmful gas emissions [9].
To solve this problem, the use of CO as a reducing agent has been considered and investigated. NO reduction by CO is one of the important reaction mechanisms applied in three-way catalysis (TWC) designs and has attracted interest due to the simultaneous elimination of NO and CO pollutant molecules [10]. A three way catalytic converter also has the capacity to oxidize unburnt carcinogenic hydrocarbons (HC) to carbon dioxide and water [11, 12]. However, the noble metal (Pt, Pd and Rh) catalysts are expensive and have issues with thermal stability [13].

Supported metal catalysts on ceramic nanofibers potentially may provide solutions to both issues. First, the enhanced surface area of the nanofibers may allow design of catalytic converters of equivalent performance but with less total mass (and less cost) of catalyst. Second, the fiber structure, nano-dimensioned in diameter and macro-dimensioned in fiber axial length, may effectively reduce the mobility of the metal particles at elevated temperatures.

The fiber structure materials can provide a way of constructing catalyst systems that have a high surface area, light weight, and stable structure for the NO decomposition by CO reaction [14, 15]. The noble metals (Pd or Pt) supported on alumina are frequently used for catalytic performance [3, 12, 16]. Especially, the Pd catalysts offer several advantages including high activity, thermal stability, good performance as well as lower cost compared to the Pt catalysts [17-20].

In this project, palladium nanoparticles were blended into a solution of a sacrificial polymer and an aluminum sol gel precursor to form alumina fibers
containing the palladium particles. The polymer solution was electrospun into template submicron fibers. These fibers were calcined at temperatures between 650°C and 1150°C to remove the polymer and oxidize the aluminum. The crystal structures of the calcined fibers varied with the calcination temperature. The calcined fibers were formed into fibrous mats and tested for their catalytic performance.

Alloys or bimetallic heterogeneous catalysts frequently exhibit better catalytic performance (stability, activity and selectivity) in comparison to their single-metal constituents [21]. Some synergetic effects of Pd-Au alloy formation have been examined by Goodman [22-24]. It is reported that there is a challenge to achieve high dispersion of pure palladium nanoparticles [25].

In this project, Pd-Au alloy nanoparticles dispersed on TiO₂ sub micron sized fibers for NO-CO reaction and CO oxidation have been investigated, we examined different catalysts prepared by electrospinning method to understand the enhanced reaction activity compared to single metal catalyst. We further reported the influence of the presence and content of a second metal (Pd or Au) on the Pd-Au alloy nanoparticle size and dispersion.

Further experiments of electrospun ceramic fibers were applied to the biodurability study. Environmental, health, and safety concerns of nanotechnology have received attention from organizations such as the National Academies [26]. The manufacture, use, and disposal of engineered nanomaterials may lead to exposure of humans to the nanomaterials. Because these materials are relatively
new and their biological behavior may differ from that of the bulk material with the same chemical compositions, concerns exist about their potential human health effects. In particular with regard to ceramic nanofibers, there is a paucity of information concerning risk from inhalation exposure.

In this project, Al₂O₃ nanofibers were fabricated, characterized, and tested to study the physicochemical effects of the properties of small ceramic fibers, including fiber sizes, surface morphologies, crystalline phases, and surface areas with respect to submicron sized alumina fibers formed by calcination of electrospun polymeric fibers.

1.2 Problem Statement

The control and abatement of NOx emissions are important because of their harmful effects on the human body and the environment. Catalytic converters are commonly used reduce NOx gases from gasoline and diesel engine exhaust gases and from discharge gases from some industrial operations. Supported metal catalysts on ceramic nanofibers potentially may offer solutions to convert harmful gases to more environmentally friendly gases in automotive and chemical plants.

Among nanomaterials, alumina or titania ceramic nanofibers are of high interest for thermal stability in high temperature applications. From a health and safety perspective fiber materials should be evaluated for their potential to cause pulmonary diseases. In this work, we compare the biodurability of different types
of electrospun ceramic nanofibers in artificial lung fluid models and elucidate how the physicochemical properties are controlled by the production process to yield fit-for-purpose nanofibers with varying biodurabilities. Engineering parameters can be manipulated to produce fibers with most favourable biodurabilities within the constraints of the application operating conditions.

1.3 Research Objectives

This work is divided into three categories, hence, the objectives were made based on each categories. Following are objectives of this research work.

1. Biodurability study of ceramic fibers through artificial lung fluid
   - Develop and produce the ceramic fibers that obtain different crystalline structure.
   - Study the physicochemical effects of the fibers with respect to fibers formed by calcination of electrospun polymeric fibers.
   - Measure the rate of dissolution rate of the electrospun ceramic sub-micron fibers through artificial lung fluid.

2. Effect of calcination temperature on NO-CO decomposition by Pd/Al$_2$O$_3$
   - Fabricate the Pd nanoparticles supported by Al$_2$O$_3$ fibers.
   - Modify the crystal structures of the Pd/Al$_2$O$_3$ fibers with varying the calcination temperature.
   - Evaluate the catalytic performance of Pd doped alumina fiber media based calcined at various calcination temperature.
3. Pd-Au alloy particles supported by TiO2 fibers for NO-CO decomposition
   - Develop the Pd-Au bimetallic heterogeneous catalytic fiber media using electrospinning, calcination, reduction, and vacuum molding.
   - Characterize the formation of alloyed Pd-Au particles of different metal composition.
   - Study the enhanced NO-CO decomposition and CO oxidation activity compared to single metal catalyst.

1.4 Hypothesis

The hypotheses of this work are
   - Sub-micron sized ceramic fibers can be made by electrospinning method.
   - The physicochemical property (fiber size, surface morphologies, crystal structure, density, and textural property) can be controlled by the calcination process.
   - The ceramic nanofibers with Pd catalytic nanoparticles can be made by electrospinning method.
   - Catalytic particles size and crystal structure property of ceramic fiber can be controlled by the calcination process.
   - Pd-Au alloy nanoparticles doped titania ceramic fibers can be produced by electrospinning method.
   - The catalyst on the nanofibers has potential for the NO reduction and CO oxidation.
1.5 Dissertation outline

- CHAPTER I gives the background and overview of work, problem statement, objectives and hypothesis.
- CHAPTER II reviews the literature about noble metal catalysts, mechanism of heterogeneous catalysis, bimetal alloy catalysts, biodurability of nano-materials, effect of physicochemical property on the dissolution rate, and electrospinning.
- CHAPTER III explains the influence of calcination temperature on the surface area of submicron sized Al₂O₃ electrospun fibers.
- CHAPTER IV explains the effect of calcination temperature on NO – CO decomposition by Pd catalyst nanoparticles supported on alumina nanofibers.
- CHAPTER V explains the Pd – Au alloy nanoparticles supported by TiO₂ fibers for NO decomposition by CO.
- CHAPTER VI explains the CO oxidation over Pd – Au nanoparticles doped fibrous TiO₂ fiber media.
- CHAPTER VII explains the comparative dissolution study of electropsun Al₂O₃ nanofibers in artificial lung fluid.
- CHAPTER VIII explains the vertical rod method for electrospinning polymer fibers.
- CHAPTER IX presents the conclusion and future work.
- APPENDIX A presents the TiO₂ fiber characterization study.
- APPENDIX B presents the compositions of artificial lung fluids.
CHAPTER II
LITERATURE REVIEW

A review of literature on effect of calcination temperature on the ceramic fiber, toxicity of fibers, NO and CO reaction over noble metals, and catalytic reactivity of alloys or bimetallic heterogeneous catalysts are summarized in this chapter.

2.1 Effect of calcination temperature on the alumina ceramic fiber

The nanostructured alumina such as, nanorods, nanotubes, nanowire (nanofibers), and nanowhiskers, have attracted a lot of attention over the past decade because they have many advantages such as, its thermal, chemical, and physical properties for applications in catalysts, ceramics, capacitors, and substrates [27]. The continuous alumina ceramic fibers at the mass production scale have been produced since 1963 [28]. Alumina is relatively inert in the desired temperature range, relatively low cost, readily available, and has low environmental impact.
For crystalline structures of alumina, there are many crystal forms of Al₂O₃ (λ, δ, η, θ, κ, χ, γ, α) [29]. The nature of phase transformation of alumina materials strongly depends on its precursor; thus, thermal decomposition of bayerite (α-Al(OH)₃) gives the sequences η (200° - 300°C) → θ (600° - 800°C) → α-Al₂O₃ (1000° - 1100°C), while that of boehmite (γAlOOH) gives γ (300° - 500°C) → δ (700° - 800°C) → θ (900° - 1000°C) → α-Al₂O₃ (1000° - 1100°C) [30].

Among these transitions, α-Al₂O₃ is the ultimate product of the thermodynamically stable alumina structures [31]. The metastable Al₂O₃ structures can be divided into two broad categories: a face centered-cubic (fcc) or a hexagonal close-packed (hcp) arrangement of oxygen anions [29]. It is the distribution of cations within each subgroup that results in the different polymorphs [32]. The Al₂O₃ structures based on fcc packing of oxygen include γ, η (cubic), θ (monoclinic), and δ (either tetragonal or orthorhombic), whereas the Al₂O₃ structures based on hcp packing are represented by the α (trigonal), κ (orthorhombic), and χ (hexagonal) phases [30-32].

2.2 NO and CO reaction over noble metals

Catalytic conversion of automotive exhaust gas is one of the most significant issues in keeping emissions of environmental pollutants [33]. Furthermore, over 30 million tons of NOx are vented to the earth’s atmosphere each year [34]. Exhaust gas contains toxic nitrogen oxides, NOx (e.g., NO and
NO\textsubscript{2}) that are produced thermally through a gas-phase reaction of N\textsubscript{2} and O\textsubscript{2} at the elevated temperature in combustion engines [33, 34].

Catalyzed reactions are considered the most efficient and cost effective method to simultaneously eliminate NO and CO pollutant molecules form air [15]. The growing concerns for the environment have resulted in increasingly restrictive emission standards [35]. Removal of NO and CO from the exhaust streams of automobiles, power plants, and other combustion processes is a challenging task [36, 37]. These gases are byproducts of incomplete combustion of hydrocarbon fuels (HC) (gasoline and diesel) from engines [38]. Particulate matter (PM) (from diesel) is also another undesired product which also creates several toxic and hazardous substances by post reaction.

During the combustion process, very high temperatures are reached due to the generation of heat results in thermal fixation of N\textsubscript{2} in air to form NOx with concentrations in the range of 100 to 3000ppm [34, 39]. Thus, to solve this problem, the use of CO as a reducing agent have been considered and investigated because of its presence in significant amounts in combustion process, CO oxidation is carried out by NO reduction, and NO removal can be accomplished via reduction to from N\textsubscript{2} [40, 41]. NO reduction by CO is one of the important model reactions describing the operation of three-way catalysis (TWC), which is attracting more attention of catalytic researchers due to the simultaneous elimination of NO and CO pollutant molecules [10]. It is reported that a three way catalytic converter has the capacity to simultaneously eliminate three pollutants such as (1) Reduction of nitrogen oxides to nitrogen and oxygen (2) Oxidation of carbon monoxide to less
harmful carbon dioxide and (3) Oxidation of unburnt hydrocarbons (HC) to carbon
dioxide and water [11, 12].

The amount of NOx, CO and hydrocarbon emission in combustion varies,
depending on the air-to-fuel ratio (A/F ratio) [42]. Three Way Catalysts (TWC) can
effectively remove the pollutants only when the air/fuel (A/F) values are
stoichiometric at $\lambda = 1$ or $A/F = 14.6$ with an A/F ratio slightly fuel-rich of
stoichiometry [43]. It means that appropriate amounts of reducing and oxidizing
agents need to be presented in the exhaust to conduct reactions [44, 45]. If an
engine could be held at the strict stoichiometric condition for the fuel used, it is
theoretically possible to obtain 100 % conversion efficiencies.

Various catalytic schemes have been devised to remove NO from exhaust
streams. Bhattacharyya et al. (1999) reported that a reducing agent for NO is
carbon monoxide (CO) and the possible reactions over supported noble metals
such as Pt, Pd, and Rh. CO reacts initially with NO to produce N$_2$O which
undergoes further reactions with CO to yield N$_2$ and CO$_2$ (2.1 ~ 2.3) [8].

$$2NO + CO \rightarrow N_2O + CO_2 \quad (2.1)$$

$$N_2O + CO \rightarrow CO_2 + N_2 \quad (2.2)$$

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \quad (2.3)$$

Chuang et al. (1999) also proposed NO – CO reaction mechanisms on the
Pd/Al$_2$O$_3$ catalyst through the in situ infrared spectroscopy (IR) coupled with TPR.
Below the light-off temperature (i.e., 300°C), NO – CO is absorbed on the
palladium and a surface reaction produces the N₂O, CO₂ and N₂ gases as shown in Table 2.1 [46].

Table 2.1 Proposed mechanism for the NO and CO reaction [46]

<table>
<thead>
<tr>
<th>Adsorption and desorption</th>
<th></th>
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<tbody>
<tr>
<td>Pd + NO ↔ Pd – NO</td>
<td></td>
</tr>
<tr>
<td>Pd + CO ↔ Pd – CO</td>
<td></td>
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<table>
<thead>
<tr>
<th>Surface reaction</th>
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<tbody>
<tr>
<td>Pd – NO → Pd – N + Pd – O</td>
<td></td>
</tr>
<tr>
<td>Pd – NO + Pd – N → Pd – N₂O + Pd</td>
<td></td>
</tr>
<tr>
<td>Pd – CO + Pd – O → Pd – CO₂ + Pd</td>
<td></td>
</tr>
<tr>
<td>2Pd – N → Pd – N₂ + Pd</td>
<td></td>
</tr>
<tr>
<td>Pd – N₂O ↔ Pd + N₂O</td>
<td></td>
</tr>
<tr>
<td>Pd – CO₂ ↔ Pd + CO₂</td>
<td></td>
</tr>
<tr>
<td>Pd – N₂ ↔ Pd + N₂</td>
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</tr>
</tbody>
</table>

Chambers et al. (2001) showed that silica supported Pd, Pt, and Rh was investigated with the hydrolysis of isocyanic acid (HNCO) during the NO - CO - H₂ reaction [47]. Tanikawa et al. also investigated the CO – NO - O₂ reaction over Pd supported on barium fixed alumina oxide catalysts [48]. The activity of Pd / Ba / Al for CO oxidation as well as NO reduction was improved by increasing the amount of barium loading [48].

In a related study using titania as the ceramic fiber, Shahreen et al. [3] noted that NO decomposition temperature depends on the anatase phase concentration
of Pd doped TiO$_2$ fibers. Park et al. and Swaminathan et al. investigated the performance of Pd, Pt, and Rh doped sub-micron sized alumina fibers for NO reaction with CO [4, 49]. The NO and CO gas was completely decomposed in the temperature range of 225 - 400°C depending on the catalyst type, the amount of catalyst, and reaction conditions [4, 76].

2.3 Catalytic reactivity of Pd-Au bimetallic heterogeneous catalysts

Nowadays, metal nanoparticles are very important due to their wide applications in molecular electronics, photoelectronic devices, and catalysis [50-53]. Single metal and bimetals have been successfully employed as catalysts in industry. Alloys or bimetallic heterogeneous catalysts frequently exhibit better catalytic performance (stability, activity and selectivity) in comparison to their single-metal constituents [21]. Specially, Pd–Au bimetallic heterogeneous catalyst is one of the most important catalytic systems. Pd–Au catalysts are used in the industrial production of vinyl acetate (VA) [54, 55]. Pd–Au catalysts have also been successfully used to catalyze many reactions like direct H$_2$O$_2$ synthesis from H$_2$ and O$_2$ [56, 57], hydrodechlorination of Cl-containing pollutants in underground water [58], hydrodesulfurization of S-containing organics [59], hydrogenation of phenol [60], coupling of acetylene to benzene [61].

For these many applications, It has been investigated that alloying or combination of two metals (Pd-Au) can lead to materials with special catalytic properties due to three types of alloy effect, indicating (1) different elementary
reaction steps (bifunction effect), (2) the electron transfer among two metals enhance reactivity (ligand effect), and (3) the specific group of surface atoms developed by geometric growth (ensemble effect) [21, 62]. These synergetic effects of Pd-Au alloy formation have been examined by the Goodman group [22-24].

The ensemble effect is mainly a diluting effect where the catalytically more active component (Pd) is diluted by the less active component (Au). As the surface ratio of Au–Pd increases, sizes of contiguous Pd ensembles decrease and eventually all Pd atoms are separated by Au as isolated Pd monomers [22, 23, 63]. For the ligand effect in the Pd-Au catalyst, charge is transferred from Pd to Au since Au has higher electronegativity as shown in Figure 2.1. Among metals, Au has one of the largest electron affinities. Au usually gains s, p electrons, but this gain of charge is partially compensated by a depletion of Au 5d electrons [64]. This situation also applies for the Pd–Au system. Therefore, there appears to be general agreement that upon alloying, Au gains s, p electrons and loses d electrons whereas Pd loses s, p electrons but gains d electrons [23, 59, 65].

![Charge transfer](image)

*Figure 2.1 Charge transfer between Pd and Au particle.*
The Goodman group stated that Charge transfer between Pd and Au also support the reason why Au is able to fully isolate Pd: notably, there are some Coulomb Pd–Pd repulsion in bulk Pd whereas Pd–Au attraction occurs as a result of net charge transfer from Pd to Au [21, 24]. For Pd and Au catalytic particles, the d-character is much more significant than s, p-character in defining their chemisorption and catalytic properties. For Pd, gaining d electrons shifts the d band center away from the Fermi level, which leads to weaker interaction between adsorbates and surface Pd atoms [21-23, 55]. Therefore, Yuan et al. demonstrated theoretical calculations that the Pd d band for Pd monomers surrounded by Au is much lower in energy than that for Pd monolayer or bulk Pd surfaces [66].

The Goodman group reported another reason that causes the Pd d band to narrow: a lattice mismatch between Pd and Au, with Pd having a lattice constant ~5% smaller than Au [23]. Upon alloying, however, Pd has been found to adopt the lattice constant of Au [21, 67]. In this case, Pd–Pd bond length increases causing the Fermi level within the Pd d band to rise. This also enhances the atomic-like character of Pd atoms and correspondingly, weakens binding toward reactants. From both charge transfer and bond length arguments, we understand that Au is able to weaken the binding strength of Pd by perturbing its d band. However, this does not necessarily mean that Au weakens the catalytic activity of Pd. In contrast, enhanced activity of Pd within Pd–Au alloys is frequently found as compared to pure Pd [21-24].

Furthermore, the Goodman group reported that there is a challenge to achieve high dispersion of pure palladium nanoparticles because palladium and
gold are easily reduced and form large metal particles due to the physical and chemical properties of noble metals during the activation process (calcination or hydrogen process) [25]. It can cause the growth of particle size, poor metal dispersion, and low catalytic activity.

Xu Yang and coworkers have shown that the addition of gold significantly improved the catalytic activity [25, 60]. They attributed the high Pd-Au catalytic performance to the high dispersion of the active components (Pd) by adding Au and the interactions between the gold and palladium [60]. Samanta et al. also reported that particle size of Pd-Au nanoparticle seems to have a correlation with the Au amount with the alloy phase [68]. Metal dispersion is defined as the ratio between surface and total metal atoms. It is an important parameter for several catalytic reactions and generally has to be as high as possible [69].

The effects of gold on/in palladium have been extensively examined by several groups [22, 23, 25, 58, 63, 70]. First, the Goodman group reported that Au atoms adjust Pd atoms in model bimetallic compounds via an "ensemble effect" that enhances catalytic performance [22]. An enhanced activity arise from geometric effects associated with high dispersion of the active components and interactions between the gold and palladium [71]. The effect of gold not only improves resistance to particle sintering but also modifies the geometry and electronic properties of the active species [72]. The addition of Au modifies the electronic property of Pd surfaces due to crystallographic alloying. CO is supposed to be preferentially adsorbed on Pd surrounded by Au atomic ensembles [70]. And then, changes in CO-Pd and O-Pd bond strengths may kinetically favor CO
oxidation [73]. As a result, a large number of Pd active sites may be created in alloy surfaces, especially by the interaction with Au atoms [73].

Prati’s group investigated the ensemble effect of Pd monomer isolated by Au, which showed Au immobilization for particle size control [74]. It has been established that the particle size effect has only limited influence on the activity of the catalysts. Therefore, Au particle formation is essential to the final shape, surface exposure, and Pd dispersion of the particles [74]. The well-alloyed particles have a large (111) surface area, which can be highly active with properly dispersed Pd atoms [23, 74].

In addition, the catalytic activity of Pd-Au depends on the preparation method, on the support type and on the pre-treatment procedure with the reduction of the gold particle size [75, 76]. Among these procedures, the deposition-precipitation (DP) has been known as the most suitable method for making small gold particles [77]. For Au atoms of Pd-Au system, oxygen activation is expected to occur directly on the small size of gold particles [78].

2.3.1 Acetylene trimerization catalytic reactions over Pd-Au models

Acetylene trimerization (3C$_2$H$_2$ - C$_6$H$_6$) is an interesting model reaction as it occurs in (UHV) ultrahigh vacuum conditions on Pd single crystal surfaces and on the increase of pressures on supported Pd catalysts [21]. Acetylene coupling have been chosen as the test reaction via Au/Pd bimetallic
colloid particle because (i) in this case Pd is very active and Au is totally inert, (ii) a range of products may be produced, and (iii) catalytic behavior is known to be sensitive to both the structure and composition of the metal surface [67].

The catalytic activity of Pd/Au surface alloys on Au(111) toward acetylene cyclization has been studied as a function of surface morphology and composition [79]. Core-level spectra indicate that electronic perturbation of Pd by Au is insignificant and the Au/Pd surface alloy behaves as a very effective catalyst. The principal effect of Au atoms at the surface is to modify the ensembles available for reactant and product adsorption, influencing conversion of the former and strongly enhancing the desorption rate [21, 79]. Richard M. Lambert and coworkers have reported that higher annealing temperatures induce more Au diffusion into the Pd bulk; therefore, simply by varying the annealing temperatures, surface alloys with different Pd–Au ratios are formed [61, 71]. In terms of reactivity, benzene forms and desorbs at much lower temperatures over the alloy surfaces than Pd(111) or pure Pd overlayers on Au(111) [21, 67].

2.3.2 Vinyl acetate synthesis over Pd-Au models

Acetoxylation of ethylene on silica-supported bimetallic Pd–Au catalysts promoted with potassium acetate is a well-established commercial route for synthesis of vinyl acetate (VA), given by the following reaction: CH₃COOH + C₂H₄ + 0.5O₂ → CH₃COOCH=CH₂ + H₂O [24, 55, 80]. Compared with pure Pd, the addition of Au has been seen to significantly improve reaction rates while also
moderately increasing the reaction selectivity [54]. Chen et al. reported that Acetoxylation of ethylene to vinyl acetate (VA) was used to investigate the mechanism of the promotional effect of Au in a Pd–Au alloy catalyst [80]. The enhanced rates of VA formation for low Pd coverages relative to high Pd coverages on Au single crystal surfaces demonstrated that the critical reaction site for VA synthesis consists of two, non-contiguous, suitably spaced Pd monomers [80].

Since ethylene combustion should include C–C and C–H cleavage of chemisorbed ethylene, the fact that ethylene binds much weaker on Pd–Au alloys makes it easy to understand why VA selectivity is higher on a Pd–Au alloy catalyst [21, 54]. Lambert group reported that VA formation rates were found to be more than 10 times faster on Pd–Au catalysts by using silica-supported Pd and Pd–Au (2.5:1 wt% ratio) alloy catalysts at reaction conditions mimicking those used in the industrial process [54]. This effect was initially assigned to a ligand effect where the weaker binding between reactants with the alloy surfaces is expected to yield faster coupling; and the weaker binding between the product VA with the alloy surfaces facilitates its desorption [54].

2.3.3 Carbon monoxide oxidation over Pd-Au models

High surface area supported Pd are outstanding catalysts for CO oxidation (CO + 0.5O_2 \rightarrow CO_2). While Au nanoparticles supported on TiO_2 material are specifically active for low temperature CO oxidation, bulk gold is inert [21]. The reason can be shown to understand: as a Langmuir–Hinshelwood type of reaction,
chemisorbed CO should react with a chemisorbed active oxygen species to form CO2 [21, 81]. The inertness of bulk gold is due to its inability to activate di-oxygen. Indeed, if atomic oxygen is pre-adsorbed onto planar Au, low-temperature CO oxidation does occur facilely [81].

Most likely oxide vacancies are formed near to the gold-support interface offering a site for oxygen adsorption [72]. Basically, CO oxidation fundamentally proceeds through the Langmuir-Hinshelwood mechanism and co-absorption of both CO and active oxygen is the most principal step [82]. The Goodman group tested Pd-Au catalyst CO oxidation as a Langmuir-Hinshelwood type of reaction [21-24, 55]. The Goodman group demonstrated that a sufficient amount of Pd segregates to the surface and generates contiguous Pd sites, which are capable of dissociating O2 to allow the CO2 formation reaction [21, 22]. Moreover, Addition of Au can weaken CO binding energy due to the charge transfer from Pd to Au [21, 68]. Thus, Pd-Au alloys can perform the CO oxidation more efficiently than pure Au and pure Pd catalyst at low temperature.

Zhang et al. performed the density functional theory (DFT) calculations to investigate CO oxidation on Pd(111) and Pd–Au bimetallic (111) surfaces to gain insights into the Au-induced ligand effect and strain effect on the catalytic activity of Pd [83]. They demonstrated that the Au surface in the Pd16Au4 slab remarkably reduces the energy barrier to 0.21 eV, in which the Au-induced ligand effect is dominant and surface Au atoms electronically promote the Pd catalyst [83]. In conclusion, the key to obtaining an active Pd–Au bimetallic nanoparticle catalyst is to prepare nanoparticles with a [Pd](Au) core/shell structure.
2.4 Toxicity of fibers

Fibers have been used extensively for industrial and construction purposes and are in widespread use. However, the production, use of fibers and materials containing fibers produces the potential for release of respirable fibers that can be inhaled and could have adverse health effects [84, 85].

Many reviews of the relevant literature on ceramic fibers stated that it can be respirable to deep regions of human respiratory tract and cause the lung tumors, and carcinomas in progress of time as shown in Figure 2.2 [86].

![Figure 2.2 Development of lung carcinoma due to epithelial fiber bombardment.](image)

(A) fiber deposition, (B) development of malignant cells, (C) aggregation of cells and tumor formation, and (D) tumor growth with final carcinoma [86].

The situations in which a worker can be exposed to ceramic fibers have occurred in the manufacture, processing, installation, and removal of ceramic
fibers or fibers containing products [85]. The National Institute for Occupational Safety and Health (NIOSH) has reviewed data characterizing occupational exposure to airborne ceramic fibers and information about potential health effects obtained from experimental and epidemiologic studies [87].

Following the epidemic of disease that arose from the use of fibers in the mid to late 20th century, there has been considerable growth and development in the use of other fiber types [88]. The World Health Organization (WHO, 1985) defined fibers as particles with the following dimensions: length > 5 μm, width < 3 μm, aspect ratio > 3:1 [89]. It was a key factor in understanding differences in the pathogenicity of fibers [88, 89]. Respirability is the fraction of the concentration of fibers that can be inhaled into the lower lung, that is, penetrate into the alveolar region of the lung. The major determinant of respirability is the fiber’s aerodynamic diameter, \(d_a\). The dimensions of the fiber (length and diameter) are important factors of fiber pathogenicity for the aerodynamic diameter, \(d_a\) [90].

Oberdörster et al. (1995) showed that respirability is about 100% for aerodynamic diameter, \(d_a\) values below 1 μm [Figure 2.3(C)], 50% respirability for \(d_a\) of approximately 4 μm [Figure 2.3(B)], and zero respirability for a \(d_a\) of approximately 9 to 10 μm [Figure 2.3(A)] [91]. However, Morgan et al. (1980) reported that all respirable fibers are not deposited in the lung [92]. From 40 to 80% fibers of \(d_a\) below 1 μm that are inhaled into the human lower lung travel back out with the exhaled air [92]. Hence, the fibers of \(d_a\) the range of 1 to 6 μm are of the greatest concern.
Maxim et al. (2006) derived a correlation between respirability and aerodynamic diameter, $d_a$. The upper limit on $d_a$, is $\sim 3-5\mu m$ for the rat lung and $\sim 6-10\mu m$ for the human lung [90]. As mentioned above, the maximum aerodynamic diameter fiber size does not penetrate into the lower lung in high enough concentrations to be of concern.

The aerodynamic behavior of the fibers, as related to the deposition of fibrous aerosols in the lung, is an important subject in view of the health implications of the fiber deposited in the pulmonary compartment. Burke et al. (1978) showed that the primary parameter governing fiber sedimentation is the fiber diameter; the fiber length is of secondary importance [93]. The aerodynamic diameter depends on the flow regime of the gas around the particle [93]. Thus, the
movement and deposition efficiency of inhaled fibers and particles can be described [94].

As Figure 2.4 shows, the aerodynamic diameter is defined as the diameter of a unit density of a sphere with a standard density (1g/cm$^3$) that has the same settling velocity as the fiber. The aerodynamic diameter differs from the physical diameter of the fiber because it also takes into account the fiber length.

Terminal settling velocity ($v_{TS}$) is a measure of the aerodynamic properties of the particle. Terminal velocity is obtained when the gravitational force ($F_G$) is equal and opposite to the drag force [95, 96].

$$F_G = m_p \cdot g = \rho_p \frac{\pi}{6} d_{ve}^3 \cdot g = \frac{3\pi\eta v_{TS}d_{ve}X}{C_C(d_{ve})} = F_{drag} \quad (1)$$
\[ v_{TS} = \frac{\rho_p d_{ve}^2 C_C(d_{ve}) \cdot g}{18 \eta \chi} \]  

(2)

where, \( m_p \) = the particle mass, \( d_{ve} \) = volume equivalent diameter, \( \eta \) = gas dynamic viscosity, and \( \rho_p \) = particle density

As stated above, the aerodynamic diameter, \( d_a \) refers to the diameter of a unit density sphere with identical terminal settling velocity (\( v_{TS} \)) as the particle. In equation (1), \( \rho_p \) is standard density (\( \rho_0 \)), \( \chi = 1 \), and the diameter is \( d_a \).

For dynamic shape factor, \( \chi \), it is almost greater than one for irregular particles and equal to one for spheres. This shape factor is used with the slip correction factor as an additional correction in equation (1) [94]. The force balance in Equation (1) can then be expressed as

\[ F_G = m_p \cdot g = \rho_0 \frac{\pi}{6} d_a^3 \cdot g = \frac{3\pi \eta v_{TS} d_a \chi}{C_C(d_a)} \]  

(3)

\[ v_{TS} = \frac{\rho_a d_a^2 C_C(d_a) \cdot g}{18 \eta} \]  

(4)

By combining equation (2) and (4),

\[ v_{TS} = \frac{\rho_p d_{ve}^2 C_C(d_{ve}) \cdot g}{18 \eta \chi} = \frac{\rho_a d_a^2 C_C(d_a) \cdot g}{18 \eta} \]  

(5)

the aerodynamic diameter can be written as

\[ d_a = d_{ve} \sqrt{\frac{1}{\chi} \frac{\rho_p C_C(d_{ve})}{\rho_0 C_C(d_a)}} \]  

(6)
with \( d_{ev} \), \( \chi \), \( C_C(d_{ev}) \), \( C_C(d_a) \), \( \rho_p \), and \( \rho_0 \) denoting, respectively, the volume equivalent diameter, the dynamic shape factor, the Cunningham slip correction factor for particles with \( d_p \), the correction factor for particles with \( d_a \), the density of the particle (g\text{cm}^{-3}), and unit density (1.0\text{gcm}^{-3}) [94, 97].

The Cunningham slip correction factor, \( C_C \), is

\[
C_C = 1 + \alpha Kn , \quad \text{Where } \alpha = \left( A + B \exp \left( -\frac{C}{Kn} \right) \right)
\]  

(7)

where \( \alpha \) is the slip correction constant in the continuum regime and the particle Knudsen number, \( (Kn = \lambda / R) \), where \( \lambda \) is mean free path of the gas molecule and \( R \) is diameter of the particle. The Slip correction factor is needed because the particles are small enough to "slip" between air molecules without collision. Thus, \( C_C \) gets larger as the particle sizes decrease. In equation (7), A, B, and C should be determined experimentally [98].

ICRP (International Commission on Radiological Protection) Research Group (1994) assumed the air conditions of the HRT (Human respiratory tract), i.e. 100\% relative humidity, 76cm Hg atmospheric pressure, an air temperature of 37\(^{\circ}\)C, and a related mean free path of the air molecules of 0.0712µm [99]. Thus, Cunningham slip correction factor, \( C_C \) is calculated by using this equation.

\[
C_C = 1 + \frac{1}{76d} [13.571 + 4.312 \exp(-7.7672d)]
\]  

(8)
In equation (6), the volume equivalent diameter, $d_{ve}$, represents the diameter of a sphere with the same volume as the particle considered for deposition calculation. In this case of a fiber with cylindrical shape, it is obtained from this formula [97].

$$d_{ve} = \sqrt[3]{\frac{3}{2} \frac{d_p^3}{\beta}}$$  \hspace{1cm} (9)

where $d_p$ represents the physical diameter of the fiber and $\beta$ is the ratio between length and diameter of the fiber. In terms of the aerodynamic diameter and actual length of small fiber, Figure 2.5 shows sedimentation mechanism in the human respiratory tract [100].

![Diagram of human respiratory tract with fiber deposition regions](image)

Figure 2.5 Fiber deposition in proximal and terminal airways of the human Respiratory Track [100].

The effect of fiber characteristics on lung deposition, clearance, and pulmonary response should be systematically evaluated to establish the true
biological effect of high aspect ratio nanomaterials [101-104]. For micron-scale fibers, the accepted paradigm is that toxicity is determined by the fiber dose, dimensions, and durability [105, 106]. The lung dose delivered over time is determined by fiber deposition (respirability) [90, 107, 108].

The dominant factor that controls fiber respirability is the aerodynamic diameter, which controls the transport and deposition efficiency of the fibers in different regions of the lung as shown in Figure 2.5 [90]. The fiber durability or biopersistence is the retention of fibers in the lung, over time, with regard to number, dimension, surface area, chemical composition, and similar physical characteristics [107].

A fiber is considered biopersistent if the rate at which it dissolves via chemical dissolution is slow relative to the rate of physical removal from the lung by mechanical action (alveolar macrophage and mucocilliary-mediated clearance) in Figure 2.6 [109]. In the non-ciliated alveolar (gas exchange) region of the lung, a primary mechanism for clearance of fibers is engulfment by alveolar macrophages (AM) and movement of the fiber-laden cells to the ciliated bronchioles [59]. A macrophage is a type of phagocyte, which is a cell responsible for detecting, engulfing and destroying pathogens and apoptotic cells. [110]. For the AM to be effective in removing fibers (Figure 2.5), the fibers should be completely engulfed by the AM. If the fibers are too long, the process is not effective or frustrated. Short fibers, less than about 15 to 20μm in length, are more easily cleared from the lungs by the AM and mucociliary transport than longer fibers [106].
Figure 2.6 Schematic exhibiting the basic histology of the bronchial (A), bronchiolar (B), and alveolar lung region (C) and the main mechanisms of fiber clearance: (1) mucociliary clearance, (2) uptake by alveolar macrophages, (3) transepitelial clearance [86, 91, 106, 108].

Long fibers can be removed if they dissolve and break into small fibers. Transverse breakage transforms long fibers into short ones, which may be cleared by AMs and reduce their biological reactivity. Long fibers are more difficult to remove from the lung and are of primary health concern. The released long fibers are deposited on the type-I and type-II pneumocytes with reaching of the alveolar interstitium (Figure 2.6(C)). Besides the mucociliary clearance taking place within the first 24 hours after exposure to the fibers, a part of the fibers deposited is subject to slow clearance mechanisms including the uptake of fibers by Type-1
and Type-2 Epithelial cell, as well as the temporary storage of the particles in the periciliary liquid layer as shown in Figure 2.6 [86, 100]. Biopersistent fibers that remain in the alveoli for an extended period of time can cause harmful effects in humans [90, 106, 108, 110].

2.5 Electrospinning

The electrospinning technique provides a simple and highly adaptable method for the fabrication of nanofibers with diameters ranging from a few nanometers to a few microns [111, 112]. A wide range of polymers, composites, and ceramic precursor solutions can be electrospun on the collector. Using this technique, hundreds of varieties of polymer and composite ceramics nanofibers are successfully produced [113, 114]. As shown in Figure 2.7, the laboratory electrospinning setup consists of four major components: syringe pump, power supply, grounded collector, and syringe with needle. A polymer or composite solution is loaded into the spinneret connected with plastic syringe. With the use of a syringe pump, the solution can be fed through the spinneret at a constant and controllable rate at the tip of the needle. An electric field is applied to the needle [115]. When the voltage is high enough to overcome the surface tension forces of the drop, a charged jet of the solution is ejected from the tip of the Taylor cone and travels towards the collector, stretching as it moves away from the needle. As the jet passes through the air the solvent evaporates, leaving a solid polymer behind [116, 117].
Many parameters for electrospinning process influence the fiber diameter such as gap distance between needle and collector, polymer flow rate, and the applied voltage. One of the most effective parameters for controlling the fiber diameter is the concentration of polymer in the solution. A list of many of the important parameters and their effects on electrospinning are summarized in Table 2.2.
Table 2.2 Cause and effect of electrospinning process parameters [115, 118].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effects</th>
</tr>
</thead>
</table>
| Gap distance                | Inversely proportional to bead formation density  
Inverse to the electric field strength  
Inversely proportional to fiber diameter |
| Flow rate                   | Directly proportional to the electric current  
Directly proportional to the fiber diameter  
Inversely related to surface charge density  
Inversely related to volume charge density |
| Voltage                     | Inversely proportional to surface charge density  
Direct effect on bead formation  
AC potential improved fiber uniformity  
Inversely related to fiber diameter |
| Concentration of polymer    | Directly proportional to the fiber diameter  
Power law relation to the fiber diameter  
Cube of polymer concentration proportional to diameter |
| Ionic strength              | Directly proportional to charge density  
Inversely proportional to bead density |
| Solvent                     | Effects volume charge density  
Directly related to the evaporation and solidification rate |
| Temperature                 | Inversely proportional to viscosity  
Uniform fibers with less beading  
Viscosity Parabolic relation to diameter, and spinning ability |

For the multiple jet electrospinning, this set-up is used for increasing the production rate. A long pipe with 20 holes [Figure 2.8(B)] is able to fabricate approximately 0.5g/h of nanofibers. Fiber production rate can easily be scaled by increasing the pipe length and the number of holes [119].

This spinning process is the same as the single spinning process. This equipment is composed of a pipe with holes, an electrode, a power supply, a grounded collector, and a reservoir as shown in Figure 2.8. The electrode is inserted into a pipe with holes to induce an electric charge into a solution [Figure
2.8(C)]. A solution is loaded into the reservoir which connects to the pipe. The multiple pendent drops are formed at the opening holes [114, 119, 120]. After the applied electric field overcomes the surface tension of the pendent drops then the drops change the shape to Taylor cone and start launching from the cone toward to a grounded collector [111, 117]. In this project, this process will be conducted to make ceramic fibers because a large amount of fibers are needed to grind them well in a mortar and pestle.

Figure 2.8 (A,B) Multiple-electrospinning set up. (C) Image of wire electrode inserted inside the pipe.
CHAPTER III

INFLUENCE OF CALCINATION TEMPERATURE ON THE SURFACE AREA OF SUBMICRON SIZED Al₂O₃ ELECTROSPUN FIBERS

3.1 Objectives

In the present study, polymer templating is used with electrospinning and thermal treatment to produce submicron size fibers. The goal of this work is to produce electrospun alumina fibers calcined at different temperatures and to better understand the influence of thermal treatment on the resulting crystal structure and surface areas.

3.2 Introduction

Alumina is among the most studied ceramic materials for catalyst support [4, 121]. It is relatively inert and low cost, readily available, and has low environmental impact. Alumina is known to exist in a number of crystal phases including λ, δ, η, θ, κ, χ, γ and α phases [30, 122, 123]. As a catalyst support, the gamma phase (γ-Al₂O₃) is the most widely used for its favorable morphological
properties (surface area, pore volume, and pore size) and acid–base characteristics [124, 125].

For the preparation of γ-Al₂O₃ nanoscale materials, various methods are reported including precipitation [126, 127], emulsion evaporation [128], and polymer templating [129]. Polymer templating is applied here with electrospinning and thermal treatment to produce submicron size fibers with change of the surface areas. The production of electrospun γ-Al₂O₃ fibers may be more economical and may produce narrow fiber size distributions than current commercial methods to produce these fibers [3].

Alumina fibers have been produced using different spinning processes [130]. Thermally stable alumina fibers having high surface areas are desired [131]. Acosta et al. synthesized γ-Al₂O₃ gelatinous materials with surface areas on the order of 130 m²/g at 1000°C from aqueous solutions of aluminum chloride in the presence of cationic surfactant molecules [132]. Fan et al. produced γ-Al₂O₃ fibers calcined at 800 and 1000°C with 128 and 125 m²/g of surface area [133]. Noguchi et al. synthesized γ-Al₂O₃ nanoparticles in supercritical water at temperature ranging from 400 to 500°C [134].

The goal of this work is to produce electrospun alumina fibers calcined at different temperatures to relate the thermal treatment, the crystal phase transformations, and the specific surface areas.
3.3 Experimental

A 9 wt% solution of polyvinylpyrrolidone (PVP, Aldrich, St. Louis, MO, \(MW: 1,300,000\)) was prepared by dissolving in ethanol (AAPER alcohol, 200 proof). An aluminum precursor solution was prepared using formic acid, aluminum acetate (basic hydrate, \((\text{CH}_3\text{CO}_2\text{)}_2\text{AlOH}_x\text{H}_2\text{O}, \text{Alfa Aesar})\), and distilled water at a weight ratio of 1:1:2.5, respectively. This mixture was well stirred. The PVP solution was mixed with the aluminum precursor solution for 1 hour to achieve complete dissolution.

Nonwoven mats were electrospun by a porous hollow tube electrospinning technique. The electrospinning device was composed of a \(\frac{1}{2}\) inch PVC pipe with an array of holes, an electrode, a power supply, a grounded collector, and a reservoir [113, 114]. The electrode was inserted into the PVC pipe to induce an electric charge into the solution. The electrospinning solution was loaded into the reservoir from which the solution flowed to the pipe [114, 119]. Multiple pendent drops were formed at the holes in the pipe. An applied voltage of about 30 kV DC, high enough to overcome the surface tension of the pendent drops, changed the drops’ shapes to those of Taylor cones [111, 117] from which jets of solution launched towards the grounded collector.

The electrospun polymer fibers were calcined in air to convert the polymer/precursor mixture to alumina ceramic fibers [135]. The fibers were heated using different temperature profiles to obtain different textural properties and
crystalline structures. The calcination profiles for the various soak temperatures are shown in Figure 3.1.

For structural characterization of the Al$_2$O$_3$ fibers, an X-ray diffractometer with a Cu anode (K$_{a1}$ = 0.154056 nm) (Bruker AXS Dimension D8 X-Ray System) was used to determine the crystal phase, crystallinity, and crystal size of the Al$_2$O$_3$ fibers. The voltage was set to 40 kV whereas the current was set to 40 mA. The crystallite size of the alumina fibers was estimated using the Scherrer equation, which relates the full width at half maxima (FWHM), $W$, of the most intense peak (440) of γ-Al$_2$O$_3$ fiber to the angle of incidence, $\theta$, via $S=c\lambda/W\cos\theta$. The percent crystallinity of fibers was calculated using the Segal equation, which includes the ratio of the most intense peak (440) from the crystalline peaks to the sum of the crystalline and amorphous intensities, $X_{CR}=I_{(440)}/(I_{(440)}+I_{(amorph)})$ [136].
Figure 3.1 Temperature profiles of the variations in the heating cycles to calcine the alumina precursor – PVP fibers to fabricate the Al$_2$O$_3$ fibers. Variation in soak temperatures (Samples labelled S650 – S1000).
Alumina fiber density was measured using helium pycnometry, which is the pycnometer instrument (AccuPycII 1340, Micromeritics) operated using research grade helium at 15.0 psig. Prior to performing density measurements, the instrument was calibrated in accordance with the manufacturer instructions using a 0.1 cm$^3$ combination sample cup/insert. Each empty sample cup was weighed to 0.1 mg precision using a calibrated microbalance (Mettler Toledo) then loaded with a sample powder. The cup with powder nanofiber samples were placed in an oven at 100 °C to dry overnight and placed in a dessicator to allow to cool to ambient temperature in a dessicator. The chamber was purged 10 times to remove moisture inside of the instrument before measurement. A total of 25 consecutive volume measurements were made with the equilibration rate set at 0.0005 psig/min and the results normalized by dry sample mass to calculate density with units of g/cm$^3$. The Brunauer, Emmett and Teller (BET) method was used to measure the surface area using nitrogen gas adsorption (Micromeritics Corp., Tristar Norcross, GA). A value of 0.162 nm$^2$ was used for the molecular cross-sectional area of N$_2$ at 77 K.

The external surface area was calculated using

$$ESA = \frac{\text{Area}_{\text{fiber}}}{\text{mass}_{\text{fiber}}} = \frac{\pi DL}{\rho_{\text{fiber}} V_{\text{fiber}}} = \frac{\pi DL}{\rho_{\text{fiber}} \pi \left(\frac{D^2}{4}\right) L} = \frac{1}{\rho_{\text{fiber}} D}$$

(1).

where $ESA$ is the calculated external surface area of the calcined alumina fibers, $\rho_{\text{fiber}}$ is the density of the fibers measured by helium pycnometry, $D$ is average
fiber diameter determined by SEM and FibraQuant 1.3 software, and \( L \) is the fiber length.

An FEI Technai F30 high-resolution transmission electron microscope (HRTEM) operating at 300 kV, a transmission electron microscope (TEM, JEM 1200XII), and a scanning electron microscope (SEM, HITACHI TM300 at 15kV) were used to study fiber sizes and morphologies. SEM images were analyzed using FibraQuant 1.3 software (nanoScaffold Technologies, LLC) to determine fiber diameter distributions. Fiber diameter distributions were plotted as curves generated out of at least 1000 measurements. Selected area electron diffraction patterns (SAED) were also recorded with the HRTEM (JEM 1200XII).

3.4 Summary and discussion

Example SEM images of calcined alumina submicron fibers are shown in Figure 3.2 (A-G). Figure 3.3 show the fiber diameter distributions measured for fibers at each calcination set point temperature to determine the temperature effects on the fiber diameters and morphologies (Figure 3.2). Each distribution of the fibers diameter was measured from at least 10 SEM images (over 8000 fibers) of one sample with different position of the fiber mat. The plot in Figure 3.2(H) shows bar chart comparing the average fiber diameters as a function of calcination temperature.
Figure 3.2 SEM images and fiber average diameter of alumina fibers calcined at (A) 650°C, (B) 750°C, (C) 800°C, (D) 850°C, (E) 900°C, (F) 950°C, (G) 1000°C, (H) Average diameter of alumina fibers corresponding to the fiber diameter distribution curves in Figure 3.3. Figure (H) include stdERR bar. significant facter ($p = 0.00000001$). Total measurements = 7162 fibers
The distribution plot (Figure 3.3) shows that all fiber sizes were in the range of 100nm - 700nm. The fibers heated at 900 - 1000°C had narrower distributions in the size range of 100nm to 300nm. The average fiber size generally decreased as the calcination temperature increased. The uncertainty bars in the plot in Figure 3.2(H) show one standard deviation in the average fiber size. The average fiber diameter at 1000°C shows a slight increase compared to 950°C but this is considered insignificant when compared to the uncertainty bars. This trend demonstrates that the different heating profiles, calcination soak temperature in particular, directly affected the diameters and distributions of the calcined fibers.

![Graph showing fiber size distribution](image)

Figure 3.3 Fiber size distribution data. These distribution curves correspond to the SEM images of Figure 3.2.

For the explanation of the difference among these fiber size distribution curves, One-way ANOVA analysis was carried out. The P-value was very close to
0 which is much less than $\alpha=0.05$, the test concludes that the calcination temperature influences the distribution of fiber diameter significantly.

The XRD patterns of the alumina fibers are plotted in Figure 3.4. The XRD patterns of the alumina ceramic fibers calcined at 650°C shows that these fibers are amorphous. As the calcination temperatures increased from 650 to 1000°C, the $\gamma$-Al$_2$O$_3$ phase peaks were observed to appear and increase in intensity for temperatures 750°C and above. The crystalline planes corresponding the $\gamma$-Al$_2$O$_3$ peaks were indexed. These samples indicate major peaks at 2$\theta$ values of 32.65°, 37.59°, 39.66°, 45.98°, 61.01°, and 67.07°, which correspond to $\gamma$-Al$_2$O$_3$ (220), (311), (222), (400), (511), and (440) crystal planes, respectively [122, 137, 138].
The XRD data of fibers calcined at 850°C show typical XRD patterns of γ-Al₂O₃, which have the highest percent of crystallinity with the most intense peaks. During the calcination process, phase transformation started from amorphous to gamma phase, and the crystallinity of the samples was also increased from 48.9% (750°C) to 80.2% (950°C) as shown in Table 3.1. In comparison with the crystalline peaks of the fibers heated at 850°C, the alumina fibers calcined at 1000°C presented some decrease in the peak intensities (440), showing a progressive transition from γ-Al₂O₃ crystal phases. Furthermore, there is a proportion of diffraction peaks, which are attributed to α-Al₂O₃ (Figure 3.4 and Table 3.1).

The appearance of the α-Al₂O₃ peaks (1000°C) indicates a partial phase transformation in crystal structure of the alumina as the calcination temperature increased. Thus, the initial α crystal phase process was involved with the formation of gamma crystal phase in the starting crystal phase material. For the fibers heated at 1000°C, the gamma crystallinity (%) decreased from 80.2% to 58.3% while the alpha crystallinity increased to its initial 31.8% with 12.2nm of crystallite size. In the calcination temperature range of 750 - 950°C the γ-Al₂O₃ crystallite size was about 8nm.

Table 3.1 shows the density of the fibers increased with calcination temperature, which was also related to agglomerated grains on the surface of the alumina fibers calcined with the elevated temperature (up to 1000°C). The increase of density with the partial phase transformation from gamma to alpha alumina is consistent with density measurements of alumina nanoparticles [139].
The TEM images of Al$_2$O$_3$ ceramic fibers (Figure 3.5) show the surface morphology of Al$_2$O$_3$ fibers. The amorphous fibers calcined at 650°C have smooth surface, whereas, gamma alumina fibers (750-950°C) appear to have produced a rougher surface morphology. The apparent roughness of fiber surface in Figure 3.5 (C, D) corresponds with the increase in crystallinity of the alumina during the calcination. Contrast in bright field and dark field of TEM images (Figure 3.5) shows the variations in intensity of diffraction across the fiber samples. The higher the crystallinity increase, the darker the contrast become (The bright field imaging mode). In this mode of the contrast, the contrast formation is formed directly by absorption of electron in the fiber sample. Thicker regions of the fibers with a higher atomic number appear dark.

The changes in surface structural features can be attributed to a difference in crystal formation and transformations from amorphous to γ-phase of alumina fibers.
Figure 3.5 TEM images of alumina fibers calcined at (A) 650°C, (B) 750°C, (C) 850°C, and (D) 950°C.

Figure 3.6 shows TEM Images of $\gamma$-Al$_2$O$_3$ fibers calcined at 850°C. The rectangular region (B) of Figure 3.6 (A) was magnified to study the lattice fringe areas using selected-area electron diffraction (SAED). The crystallinity of the $\gamma$-Al$_2$O$_3$ fibers was confirmed by SAED, which revealed three broad diffraction rings corresponding to the (222), (400), and (440) reflections in Figure 3.6 (C). The HRTEM images clearly show that the lattice fringes for the $\gamma$-Al$_2$O$_3$ phase appear in Figure 3.6 (D,E) and the interplanar spacing deduced from the image is ~0.24nm, which correspond to the (311) plane of $\gamma$-Al$_2$O$_3$ fibers. The SAED pattern and the HRTEM images [Figure 3.6 (D,E)] also show lattice spacing of 0.14nm and 0.19 nm that are consistent with the (440) and (400) planes of gamma alumina structure [141, 142].
Figure 3.7 shows nitrogen adsorption-desorption isotherms and Barret-Joyner-Halenda (BJH) pore size distribution curves of the alumina fibers. It was calculated of pore size distribution curves [Figure 3.7(B)] from experimental isotherms [Figure 3.7(A)] using the Kelvin model \[ r_{\text{actual radius pore}} = r_{\text{Kelvin radius pore}} + t_{\text{thickness of the absorbed film}} \] of pore filling [143]. The nitrogen isotherms in Figure 3.7(A) resulted in classical type IV performance with a sharp capillary condensation step [144]. A well-defined H2 hysteresis loop with a sloping adsorption branch and a relatively steep desorption branch was observed in the range of 0.45 - 0.9 relative pressure in Figure 3.7(A). Additionally, the pore size distribution at high pressure was assessed by the BJH model according to the desorption branch as shown in Figure 3.7(B).

Figure 3.6 TEM Images of $\gamma$-Al$_2$O$_3$ fibers calcined at 850°C.
As the calcination temperature increased from 650 to 1000°C, the position of the step gradually shifted to higher relative pressures, which reflected the effect of morphology change on the internal pore size of alumina fibers. The pore diameters were in the range of 3 – 20 nm. In contrast to the alumina fibers at 650°C, the fibers at 850 to 1000°C had broader pore size distributions and larger average pore diameters.

The textural properties of the alumina fibers are summarized in Table 3.2. An increase in the surface area (m²/g) was observed as the calcination temperature increased from 650 to 850°C, which may be related to the internal pore formation on the alumina fibers. The TEM images in Figure 3.5 showed the
fibers calcined at 650°C had apparently smooth surfaces without any changes of surface visually. In contrast, fibers calcined at 850°C had apparent highly rough surfaces and crystallized structures as shown in Figure 3.5 (C). During this transition of phase and morphology, small internal pores might be formed within the fibers at 850°C. The BET data shows the surface area increased significantly for alumina fibers heated at 850°C to 151 m²/g with 6.9nm pore width (interpreted as the pore diameter at the mouth of the pore) and 7.4nm pore diameter (average pore diameter over the length of the pore).

Table 3.2 Textural properties of Al₂O₃ fibers.

<table>
<thead>
<tr>
<th>Material</th>
<th>T_{calcine} (°C)</th>
<th>Crystal Phase</th>
<th>BET SSAᵃ (m²/g)</th>
<th>Pore widthᵇ (nm)</th>
<th>Pore diameterᶜ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>650</td>
<td>Amorph</td>
<td>8.52±0.94</td>
<td>5.72±0.07</td>
<td>4.21±0.06</td>
</tr>
<tr>
<td>Alumina</td>
<td>750</td>
<td>γ</td>
<td>108.6±1.19</td>
<td>5.12±0.12</td>
<td>4.04±0.09</td>
</tr>
<tr>
<td>Alumina</td>
<td>800</td>
<td>γ</td>
<td>119.32±0.85</td>
<td>6.78±0.09</td>
<td>5.09±0.08</td>
</tr>
<tr>
<td>Alumina</td>
<td>850</td>
<td>γ</td>
<td>151.72±0.41</td>
<td>6.86±0.04</td>
<td>7.42±0.03</td>
</tr>
<tr>
<td>Alumina</td>
<td>900</td>
<td>γ</td>
<td>57.88±0.73</td>
<td>7.47±0.15</td>
<td>7.62±0.13</td>
</tr>
<tr>
<td>Alumina</td>
<td>950</td>
<td>γ</td>
<td>44.91±0.38</td>
<td>7.24±0.09</td>
<td>8.09±0.09</td>
</tr>
<tr>
<td>Alumina</td>
<td>1000</td>
<td>γ+α</td>
<td>32.66±0.12</td>
<td>10.08±0.21</td>
<td>10.92±0.18</td>
</tr>
</tbody>
</table>

ᵃBET specific surface area, bPore width calculated by 4V/A (V=single gas adsorption total pore volumes of pores (cm³/g) and A=BET surface area), and cBJH pore diameter calculated by 4V/A (V=BJH adsorption pore volume (cm³/g), and A=BJH absorption cumulative surface area of pores (m²/g))

Upon heating above 900°C, the dramatic reduction of surface area occurred, pointing out a 78% decay of BET surface area with 11nm of pore size enlargement after 1000°C of heat treatment. Generally, the γ-Al₂O₃ phase goes through a series of transformation to reach the thermodynamically stable α-Al₂O₃ phase structure [31, 145]. Thus, the surface grain agglomerating of the alumina
fibers [Figure 3.5(D)] incurred during calcination could lead to reduction of the specific surface area. Furthermore, the calcination temperature at 1000°C might disrupt the grain growth of the γ-Al₂O₃, and then, the framework shrinkage of alumina fiber took place with a decrease of BET surface area while the pore diameter on the surface of alumina fiber increased as shown in Table 3.2. This trend of the thermally-induced surface area reduction and pore size, width expansion is consistent with observations reported in literature [146-149].

Figure 3.8 compares the trends in all of the measured data versus the calcination soak temperature. The density, the pore width, and the BJH pore diameter of the alumina fibers increased with the soak temperature, which was caused by the structure consolidation and pore enlargement. In addition, significant decreases in the surface area [Figure 3.8(C)] and the BJH pore volume [Figure 3.8(F)] at temperatures exceeding 900°C were observed, which is mainly due to the modification of pore length within the alumina fiber with the growth of the γ-Al₂O₃ crystallites during the calcination process [141, 146, 148].

When fiber average diameter dropped to 140nm with 80% of crystallinity, the external surface area was 8.5 m²/g as calculated geometrically by Area_{fiber}/mass_{fiber} (Eqn 1). On the other hand, BET measured surface areas include internal pore surfaces and external fiber surfaces, through physical adsorption of nitrogen gas. The BET surface areas increased from 8 m²/g (at 650°C) to 151 m²/g (at 850°C) and then decreased to 33 m²/g (at 1000°C) [Figure 3.8(C)]. The highest surface area (151 m²/g) at 850°C corresponds with 71% of gamma crystallinity and the average fiber diameter of about 250nm. Thus, the
changes of fiber morphology and internal pore properties on the fiber surface were due to the changes of the amount of gamma crystallinity of the fibers and, at 1000°C, the relative amounts of alpha versus gamma phase crystals in the fibers.

Figure 3.8 Comparison of all the various trends (A) fiber diameter, (B) density, (C) BET surface area, (D) pore width, (E) BJH pore diameter, (F) BJH pore volume, (G) gamma crystallite size, and (H) gamma as a function of soak temperature. Error bars are not visible when they are smaller than the symbol size.
For the comparison of all the various trends among alumina fibers calcined at 650 - 1000°C, One-way ANOVA analysis was performed to evaluate the difference with significance calculated. Since the P-value was very close to 0, which is much less than the selected α=0.05, it statistically verifies that the calcination temperature significantly affected all measured data.

3.5 Conclusions

Aluminum acetate/PVP composite electrospun fibers were prepared by electrospinning with multiple jets. The polymer fibers were converted to alumina fibers by calcining the fibers in air. As calcination temperature increased the alumina fibers compositions transitioned from amorphous to increasing crystallinity of gamma phase alumina. As the calcination temperature increased to 750°C the fibers transitioned from amorphous to 49% crystalline gamma phase Al₂O₃. The crystallinity further increased with calcination temperature to 80% gamma Al₂O₃ at 950°C, but decreased above 950°C as the crystal structure began to change to alpha phase. The fiber diameters tended to decrease as calcination temperature increased to 950°C but increased as the alpha phase was formed at temperatures above 950°C. Surface areas as measured by BET decreased as gamma phase crystallinity increased. Further decrease in surface area as the gamma phase crystal structure transitioned to alpha phase indicated changing internal pore structures of the fibers.
CHAPTER IV

EFFECT OF CALCINATION TEMPERATURE ON NO – CO DECOMPOSITION
BY PALLADIUM CATALYSTS SUPPORTED ON ALUMINIUM NANOFIBERS

4.1 Objectives

This present work focuses on the effect of the calcination temperature of electrospun fibers. The Pd/Al₂O₃ fibers were prepared over a range of calcination temperatures and tested for comparison of their performances. Little information exits in regard to the catalytic performances of the metal-support interaction in Pd/amorphous-Al₂O₃, Pd/γ-Al₂O₃, and Pd/α-Al₂O₃ catalyst with respect to Pd doped alumina fibers formed by calcination of electrospun polymeric fibers. Moreover, catalyst performance when subjected to extreme environment conditions such as high temperatures (up to 1100°C) are topics of recent research [150-152]. This chapter shows the effect of calcination temperature and the corresponding various alumina crystal phases on the catalyst performances.

4.2 Introduction

The catalyzed reaction decomposition of NO with CO gases are of significant interests for environmental and health reasons. Recent developments
in fabrication of ceramic submicron fibers provide a means to fabricate fibrous
catalyst support structures that may result in smaller catalytic converters and new
designs of catalyst support structures not available in the traditional monolithic or
pelletized bed designs. The nanoscale of the supporting fibers may provide
enhancements such as restricting the migration of metal catalyst particles.
Research on the performance of nanofiber supported catalysts is relatively new
and few data have appeared in scientific literature.

The wet impregnation process is commonly used for preparation of
supported catalysts [3, 16]. As an alternative the palladium noble metal can be
integrated within and near the surface of alumina submicron fibers by blending the
catalyst particles into the sol gel electrospinning solution thus eliminating the wet
impregnation step [4, 153, 154]. A catalyst-support structure of metal oxide
submicron fibers have a high activity due to their high surface area and are
thermally and chemically stable. The fibers have a remarkable capacity for the
attachment or release of functional groups, can support nanometer and micron
sized particles, and uniquely have nanoscale properties due to the small diameters
of the fibers but provide macroscale handling properties due to the fiber lengths
[155, 156].

The Al₂O₃ material is commonly used as a support structure for palladium
catalysts due to its optimal mechanical properties and thermal stability for high
temperature gas applications [157]. Catalyst performance when subjected to
extreme environment conditions such as high temperatures (up to 1100°C) are
topics of recent research [150-152].
4.3 Experiment

This part is going to describe the procedures for the fabrication of the fiber media and catalytic reaction test set up.

4.3.1 Materials

The aluminum precursor solution was prepared by mixing aluminum acetate (Basic Hydrate, (CH₃CO₂)₂AIOH xH₂O, AlfaAesar), formic acid, and distilled water at a weight ratio of 1:1:2.5 respectively. This mixture was well stirred overnight. A 9 wt% solution of Polyvinylpyrrolidone (PVP, Aldrich, MW: 1,300,000) was prepared by dissolving PVP in ethanol (AAPER alcohol, 200 proof). The PVP solution was mixed with the aluminum precursor solution in 1:2 weight ratio, respectively, for 12 hours to achieve complete dissolution. Palladium chloride powder (Sigma-Aldrich, 60 % Pd) was mixed into the resulting mixture in the ratio of 5 wt% PdCl₂ with respect to aluminum acetate and stirred overnight at 40 °C using a magnetic stirrer [4].

4.3.2 Fabrication of electrospun PdCl₂ / Aluminum acetate / PVP fibers

In this work, a double needle electrospinning technique was used to fabricate the PdCl₂ + Aluminum acetate/PVP composite submicron fibers. As shown in Figure 4.1, a typical laboratory setup for double needle electrospinning consists of two spinnerets with two metallic needles, power supply, syringe pump, and a rotating drum collector [114].
Two plastic syringes (BD 5 ml Syringe, Fisher Scientific) were filled with the prepared electrospinning solution and attached to the syringe pump and the power supply. The syringe pump, (SP101I, WPI), was adjusted to provide a 3 μl/min of the electrospinning solution at the tips of the 21 gauge steel needles. A 25 kV of electric voltage potential was applied to the needles from the power supply (Gama high voltage, Ormond Beach, FL). The electric field overcame the surface forces on the droplets at the tips of the needles and caused jets to launch from the droplets towards the grounded collector.

![Schematic diagram of the double-needle electrospinning setup](image)

Figure 4.1 Schematic diagram of the double-needle electrospinning setup

4.3.3 Thermal treatment of electrospun PdO / Al₂O₃ fibers

The collected electrospun submicron fibers were calcined in air to remove the polymer (PVP), to convert the aluminum precursor (CH₃CO₂)₂AlOH xH₂O) to alumina metal oxide form (Al₂O₃), and to convert the metal salt (PdCl₂) to metal oxide (PdO). Normally, PVP polymer degrades at more than 450°C. In this work, the fibers were calcined for 4 hours at 650°C, 750°C, 850°C, 950°C, 1050°C, and
1150°C with 10°C/min ramping rate in a furnace (Baker Furnace, Inc. Laboratory Oven Model 13).

4.3.4 Preparation of catalytic fiber media

Palladium catalytic fiber media were prepared by using a vacuum molding process. The custom-made vacuum mold apparatus is shown in Figure 4.2 and consisted of a mixing tank, collecting tank, Plexiglas mold, vacuum pump, and a liquid slurry. The liquid slurry contained four liters of deionized water with 0.5 g of chopped alumina microfibers (Saffil HA bulk fibers, Thermal Ceramics), 0.05 g of PdO doped alumina submicron fibers (Synthesized in this work), 0.02g of corn starch, 0.5ml of binder, and 20 drops of dilute H₂SO₄ acid. Here, diluted acid was added to maintain the slurry at a pH ~ 6.0 and starch was added in order to enhance the binding capability of binder and fibers.

Figure 4.2 Schematic diagram of vacuum molding setup
The slurry was mixed overnight using an agitator (Talboys Laboratory Stirrer with propeller paddle 2”Dia 5/16” X 12”) to obtain a uniform dispersion of materials. The slurry was placed into the mixing tank in Figure 4.2 and agitated by bubbling air into the bottom of the tank. The slurry was drained through a filter paper (Schleicher & Schuell Whatman Cat No 1113-090) supported by a stainless steel mesh in a Plexiglas mold with an internal diameter of 2.3 cm. The liquid was drawn through the mold by vacuum into the collection tank with aid of a vacuum pump. The fibers were retained on the steel mesh covered by filter paper to form a wet fibrous cake and the wet cake was heated to 600°C to dry the cake and bind the fibers together [49].

4.3.5 Reduction

PdCl₂ precursor was converted into PdO through the calcination process due to reaction with oxygen in the air. The PdO was reduced into metallic Pd nanoparticles using hydrazine by the reaction [158].

\[
\text{N}_2\text{H}_4(\text{l}) + 2\text{PdCl}_2 \rightarrow \text{N}_2(\text{g})\uparrow + 2\text{Pd}^0(\text{s}) \text{[grayish black]} + 4\text{HCl (1)}
\]

The oxidized fiber media were placed in a ceramic crucible and placed inside a hood. 3ml of hydrazine monohydrate (N₂H₄·H₂O, 98% purity) solution were added drop by drop to the media. An exothermic reaction occurred during the addition of the hydrazine solution, and the oxygen atoms were removed from the palladium
oxide form. The reduction of PdO to Pd was verified using X-ray diffraction peaks as discussed in the XRD section.

Figure 4.3 Photographs of a Palladium catalytic fiber medium (A) before reacted with hydrazine, (B) after hydrazine reaction, and (C) next to a scale showing the 2.3 cm diameter of the medium.

The catalytic fiber media were stored inside the covered crucible until the exothermic reaction stopped and all smoke from the media terminated. The colors of the media changed from brown to grayish-black. Figure 4.3 shows the images of a palladium catalytic fiber medium before and after reduction using the hydrazine.

4.3.6 Catalytic reaction set up for NO decomposition

For the reaction tests of the catalytic fiber media, three gases (He, CO and NO) were flowed through the media with controlled flow rates using three mass
flow meters (Omega FLDA3428ST, FMA 5400, FMA 5500). The reaction gases consisted of 1 mole/mole % NO, 1% CO, and 98% He, and the inlet volumetric flow rate of 100 sccm.

Figure 4.4 Flow Diagram for measuring catalytic performance experiment.

The catalytic medium was placed in a steel reactor with a 2.3 cm diameter hole to hold the test sample. The reactor was wrapped with a heating tape (Omega FGS051-060) connected to a temperature controller (Micromega CN77000). Gas concentrations before and after the reactor were measured with gas chromatography (TCD GC, SRI 8610C). Peak Simple software (Version 3.29) was used to calculate and display the peaks and concentrations of the components. In this work, each experiment was repeated three times with the same inlet flow rates and same inlet concentration ratio of the gases. A flow diagram of the laboratory set up is shown in Figure 4.4.
4.3.7 Characterization

The fiber morphologies and size distributions of fibers and catalytic particles were analyzed by SEM (FEI Quanta 200 at 30kV), TEM (JEM 1200XII) and HRTEM (FEI Tecnai G2 F20). Energy dispersive X-ray analysis, EDX (Bruker Quantax 70) were used for the elemental quantification analysis. X-ray diffractometer (Bruker AXS Dimension D8 X-ray) was used to determine the crystal structure. The Brunauer, Emmett and Teller (BET) surface areas of the fiber mats were measured using nitrogen gas adsorption. The detailed characterization explanation have been reported in the experiment section of chapter 3 and 4.
Figure 4.5 SEM images of PdO doped alumina fibers calcined at (A) 650°C, (B) 750°C, (C) 850°C, (D) 950°C, (E) 1050°C, and (F) 1150°C.

Figure 4.5 and 4.6 depicts the SEM images, diameter distributions and average diameter of PdO/Al₂O₃ submicron fibers. Each distribution of the fibers diameter was measured from multiple fibers in at least 10 SEM images. The diameters of Pd/Al₂O₃ fibers (Figure 4.6) gradually decreased with increase in the
calcination temperature. The distribution curves show most of the fibers had diameters in the range of 200 – 500nm. Figure 4.6 shows that the average diameter of the Pd/Al₂O₃ fibers gradually decreased with increase in the calcination temperature. For the explanation of the difference among these fiber size distribution curves, One-way ANOVA analysis was carried out. The P-value was very close to 0 which is much less than α=0.05, the test concludes that the calcination temperature influences the distribution of fiber diameter significantly.

Figure 4.6 Fiber diameter distributions and average diameter of PdO + Al₂O₃ fibers with calcination temperature.

Figure 4.7 (A) shows the SEM image of palladium alumina submicron fiber marked “1” and alumina micro fibers marked “2”. The submicron fibers were entrapped by the larger microfibers. Thus, this fiber structure of media by the
vacuum molding process resulted in a hierarchical fiber size structure that provides strength to the medium, support for the submicron fibers, and a porous open structure with relatively high permeability. The size of microfibers were about 3-5 μm. Figure 4.7 (B) shows the EDX spectra to quantify the elemental composition of Pd/Al₂O₃ nanofibers marked “1” in Figure 4.7 (A). The expected weight percent of palladium in the fiber media was 5 % after calcination and reduction, based on the known starting material compositions. The element summary table in Figure 4.7 (B) shows the measured amount of palladium in the fibers was very close to this, at 4.92%.

Figure 4.7 (A) SEM images of palladium doped alumina nanofibers with alumina microfiber in catalytic filter media and (B) EDX analysis of elemental composition of the circled area marked “1” in Figure 4.7 (A).

The morphologies of the fibers were observed using the TEM images. Basically, the higher calcination temperatures had produced a rougher surface morphology. During the heat treatment, the crystallite growth of the Al₂O₃
nanofibers caused significant surface roughness and was consistent with observations reported in literature [122]. The Pd particles also agglomerated together to form larger particles at the same time as shown in Figure 4.8.

Figure 4.8 TEM image of Pd doped alumina nanofiber calcined at (A) 650°C, (B) 850°C, and (C) 1050°C.

The images reveal that the Pd catalytic particles were dispersed within and near the surface of the alumina fibers. An increase of the calcination temperature may cause, the migration and agglomeration of the metal particles within the fibers.

The average particle size varied with the thermal treatment of Pd/Al₂O₃ fibers. Figure 4.8 shows the trend that the average size of the particles increased from around 4.7 ± 1.1 nm for calcination at 650°C to 21.4 ± 4.3nm for calcination at 1050°C. The larger Pd agglomerates in the fibers at higher temperatures gave a stronger signal in the XRD measurements as discussed in the next section.
The changes of Pd/Al₂O₃ fiber morphologies and the particle size were displayed in the TEM images. To determine the change of the crystal structure with the calcination temperatures X-ray diffraction analyses were undertaken. Figure 4.9 shows the comparison of X-ray diffraction peaks of PdO/Al₂O₃ fibers before hydrazine and Pd/Al₂O₃ fibers after hydrazine. It is evident from Figure 4.9 that PdO was reduced to the base metal Pd nanoparticles after reduction using hydrazine.

Figure 4.9 X-ray diffraction peaks of (A) PdO/ Al₂O₃ nanofibers before hydrazine and (B) Pd/Al₂O₃ nanofibers after hydrazine.

For PdO/Al₂O₃ spectra in Figure 4.9 (A), the diffraction peaks at 2θ = 34.3°(101), 42.4°(110), 54.3°(112), 60.1°(103) and 71.6°(202), indicate the detection of PdO. In comparison in Figure 4.9 (B) the peaks at 2θ = 40.4°, 46.9° represent the indices of (111), (200) crystal planes of Pd. No diffraction peaks corresponding to the PdO phase were observed, indicating that Pd existed in a
different crystal phase of the Pd/Al₂O₃ fibers after treatment with hydrazine. Upon the increase of the calcination temperature from 650° to 1150°, the diffraction line of Pd (2θ = 40.4°, 46.9°) became apparent and more intense, which could be ascribed to the change in crystallite size.

The average crystallite size was calculated using the Scherrer equation, which relates the full width at half maxima, W, of the most intense peak (111) of Pd phase to the angle of incidence, θ, via $S=\frac{c\lambda}{W\cos\theta}$, where $S$ is the average crystallite size, $c$ is the Scherrer constant and $\lambda$ is the wavelength of X-rays used (0.154056 nm). The Scherrer constant can take values from 0.9 to 1.2, depending on the shape of the particles. Here we assumed the spherical shape ($c = 1$). Thus, the calculated average crystallite size of Pd/Al₂O₃ nanofiber increased with calcination temperature as shown in Figure 4.9 (B). Furthermore, the diffraction lines indicative of amorphous - (650°C), γ - (750°C - 950°C), and α - Al₂O₃ (1050°C - 1150°C) phases were also observed in all PdO/Al₂O₃ and Pd/Al₂O₃ samples. It was clear that the phase transformation and the growth of Pd particle size occurred simultaneously.

The surface textural characteristics for different Pd/Al₂O₃ nanofibers samples were estimated via gas adsorption by studying the adsorption and desorption isotherms. There are six types of adsorption isotherms (Type I - VI) with respect to the IUPAC classification [144]. The nitrogen isotherms in Figure 4.10 (A) resulted in classical type IV performance with a sharp capillary
condensation step [144]. For Type IV (hysteresis loop), capillary condensation gives rise to a hysteresis loop and these isotherms also exhibit a limited uptake at high relative pressures as shown in Figure 4.10 (A) [144]. A well-defined H2 hysteresis loop with a sloping adsorption branch and a relatively steep desorption branch was observed in the range of 0.4 - 0.98 relative pressure. Additionally, the pore size distributions at high pressure were assessed by Barret-Joyner-Halenda (BJH) model according to the desorption branch as shown in Figure 4.10 (B).

Figure 4.10 (A) N2 adsorption-desorption isotherms and (B) BJH pore size distribution curves of Pd/Al2O3 nanofibers calcined at high temperature.

For Pd/Al2O3 nanofibers calcined at 650°C the capillary condensation step occurred at a relative pressure of about 0.4. As the calcination temperature increased to 1150°C, the position of the step gradually shifted to higher relative pressures, which indicated a change in the pore sizes in the fibers. The systematic increase of the pore size with the increase of calcination temperature was further
confirmed by the pore size distribution curves as shown in Figure 4.10 (B). The pore size distributions in Figure 4.10 (B) show the fibers calcined at 650°C had pores in the narrow range of 3 to 5 nm in contrast to the fibers calcined at 1150°C that had pores in a much broader distribution of about 8 to 16 nm. Such curves typically have hysteresis and pore size distributions may be ascribed to the increase of calcination temperature in control of the Pd particle size and the change of alumina crystallinity structure.

![Graph showing specific surface area of palladium doped alumina nanofibers with calcination temperature.](image)

Figure 4.11 Specific surface area of palladium doped alumina nanofibers with calcination temperature.

The specific surface areas of Pd/Al₂O₃ fiber samples were plotted in Figure 4.11. As the calcination temperature increased from 650°C to 1150°C, the surface area decreased from 58.9 m²/g (650°C) to 17.2 m²/g (1150°C). This trend of the surface area helps to interpret the catalytic performance of fiber media in the next section.
NO decomposition by CO was performed to evaluate the catalytic performance of the Pd catalytic fibrous media. The reaction temperature was varied in the range from 100°C to 500°C and reaction concentration data plotted in Figure 4.12. The inlet concentrations of the reactants, and the amounts of Pd, and catalytic materials were fixed to obtain comparable reaction kinetic information of the NO-CO reaction.
Figure 4.12 Performance of Pd doped alumina fiber media based calcined at (A) 650°C, (B) 750°C, (C) 850°C, (D) 950°C, (E) 1050°C, and (F) 1150°C.

Figure 4.12 (A, B) shows that all the nitric oxide and carbon monoxide were decomposed to nitrogen, nitrous oxide, and carbon dioxide gases at 350°C of the reaction temperature for media calcined at 650°C and 750°C. These media
correspond to the amorphous form of $\text{Al}_2\text{O}_3$ with about 5 nm of Pd particle size. Similar results were reported by Chambers et al. when the NO – CO reaction was carried out using the Pt group catalysts [47]. Granger et al. also indicated that nitrous oxide ($\text{N}_2\text{O}$) was an intermediated product in NO – CO reaction [159].

When the calcination temperature was increased to 850°C and 950°C, the simultaneous elimination of NO and CO conversion was achieved at 450°C as shown in Figure 4.12 (C, D). Interestingly, the obtained XRD results (Figure 4.9) showed that the alumina crystal structure was $\gamma$-$\text{Al}_2\text{O}_3$ nanofibers with average crystallite size $D = 9$ nm, which were dependent of the calcination temperature. Furthermore, the metallic Pd nanoparticle size (Figure 4.8) morphologically became larger. Park et al. developed a mathematical model of NO decomposition by CO regarding catalyst particle size [160]. The fitted model and experimental results for Pd catalysts are in good agreement [160] in Figure 4.13.

Figure 4.13 (A) theoretical model results for palladium doped alumina fibers with varying catalyst particle sizes and (B) comparison between the experimental (data points) and theoretical model (solid line) results [160].
Figure 4.12 (E, F) exhibit that Pd/Al₂O₃ fiber media calcined at 1050°C and 1150°C showed the lowest catalytic activity, which had a α-Al₂O₃ phase (14nm of crystallite size) with about 20 nm of Pd particle size.

For the fiber materials calcined at higher temperatures the decomposition temperature increased to about 500°C, indicating a lower reaction activity. At the higher calcination temperatures the fiber materials passed through the gamma phase and the Pd particle sizes increased. The larger particle size and possibly the change to gamma phase caused the decline in reactivity of the fiber materials.

In other words, the increase of calcination decreased with BET specific surface area, and further, caused the enlargement of the Pd particle size. NO molecules can be preferentially absorbed on the surface of the corresponding catalysts due to their unpaired electrons [15, 161]. Thus, these characterization results of Pd/Al₂O₃ nanofibers calcined with an increase temperature was not conductive to the sufficient contact between catalyst on the alumina nanofiber and NO-CO molecules [162]. Therefore, the catalytic performances of Pd/amorphous - Al₂O₃ calcined at 650°C had better conversion compared to Pd/ γ and α - Al₂O₃ calcined at 750-1150°C.
Figure 4.14 Catalytic performance of Pd doped alumina fiber media calcined at 650°C for (A) 6410 ppm, and (B) 15870 ppm of different inlet NO concentration.

The overall reaction scheme for nitric oxide and carbon monoxide can be represented by the following reaction (Equation 4.1) with mostly nitrogen and carbon dioxides gases products. N₂O is also produced as a side product in Table 4.1 [8].

\[
\text{NO} + \text{CO} = \frac{1}{2} \text{N}_2 + \text{CO}_2 \quad (4.1)
\]

Table 4.1 Moles consumed (NO and CO) and produced (N₂, CO₂, and N₂O) gases based on experimental data of Figure 4.12.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>(C_{\text{NO},O} - C_{\text{NO}})</th>
<th>(C_{\text{CO},O} - C_{\text{CO}})</th>
<th>(C_{\text{N}_2})</th>
<th>(C_{\text{CO}_2})</th>
<th>(C_{\text{N}_2\text{O}})</th>
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<td>0.19053</td>
</tr>
</tbody>
</table>
### For the media calcined at 750°C

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<th>$C_{CO,0} - C_{CO}$</th>
<th>$C_N$</th>
<th>$C_{CO_2}$</th>
<th>$C_{N_2O}$</th>
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<tbody>
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<tr>
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</tr>
<tr>
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<td>0.44697</td>
<td>0.19053</td>
</tr>
<tr>
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<tr>
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<tr>
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</tbody>
</table>

$1.04 \cdot NO + 1.12 \cdot CO = 0.57 \cdot N_2 + 0.73 \cdot CO_2 + 0.15 \cdot N_2O$

### For the media calcined at 850°C

<table>
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<th>$C_{CO,0} - C_{CO}$</th>
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<td>0.018939</td>
</tr>
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$1.05 \cdot NO + 1.13 \cdot CO = 0.57 \cdot N_2 + 0.73 \cdot CO_2 + 0.15 \cdot N_2O$

### For the media calcined at 950°C

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$1.05 \cdot NO + 1.12 \cdot CO = 0.57 \cdot N_2 + 0.73 \cdot CO_2 + 0.15 \cdot N_2O$
<table>
<thead>
<tr>
<th>Temp (°C)</th>
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<th>(C_{\text{CO},0} - C_{\text{CO}})</th>
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1.07·NO + 1.13·CO = 0.57·N\textsubscript{2} + 0.73·CO\textsubscript{2} + 0.15·N\textsubscript{2}O

For the media calcined at 1050°C

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<th>(C_{\text{CO},0} - C_{\text{CO}})</th>
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<th>(C_{\text{CO}_2})</th>
<th>(C_{\text{N}_2\text{O}})</th>
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1.04·NO + 1.12·CO = 0.57·N\textsubscript{2} + 0.73·CO\textsubscript{2} + 0.15·N\textsubscript{2}O

For the media calcined at 1150°C

<table>
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<th>Temp (°C)</th>
<th>(C_{\text{NO},0} - C_{\text{NO}})</th>
<th>(C_{\text{CO},0} - C_{\text{CO}})</th>
<th>(C_{\text{N}_2})</th>
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1.04·NO + 1.12·CO = 0.57·N\textsubscript{2} + 0.73·CO\textsubscript{2} + 0.15·N\textsubscript{2}O

In this Table 4.1, we have shown that the proposed reaction mechanism for nitric oxide and carbon monoxide [Eqn 4.1] [8] was closed to the reaction...
mechanism of the experimental data used in our study. The formation of N₂O as an intermediate product appeared in the NO – CO reaction on all fiber media samples.

The media were also tested by varying the inlet NO concentration. The flowrate of nitric oxide was changed from 6410 – 15870 ppm while carbon monoxide flow was kept constant (i.e. 31250ppm). In this work, the catalytic fiber media was correspondingly prepared Pd (5%) / Al₂O₃ catalyst calcined at 650°C.

Figure 4.14 shows the concentration profile versus reaction temperature plot with 6410ppm and 15870ppm of NO and 31250ppm of CO. There has been no significant change at 100 - 200°C reaction temperature. As temperature increased, NO was converted to N₂O and N₂. At 350°C, entire NO disappeared, including that the CO was partially converted to CO₂. Figure 4.12 (A) indicate that NO - CO reaction occurred at a lower temperature (150°C) than the NO - CO one with lower NO inlet concentration. When both NO and CO inlet concentration was the same, it was observed that both disappeared at the same temperature (300°C). It should be noted that the temperature of NO disappearance decreased with an increase of inlet NO concentration.
Figure 4.15. Exhaust gas concentrations of each product and reactant gases of palladium doped on alumina nanofibers with different calcination temperature at (A) NO conversion (%) and (B) CO conversion (%).

As another way of presenting the data, the reaction data are plotted in Figure 4.15 to show the conversions of NO and CO as a function of reaction temperature. The plots show the total conversion occurs at lower reaction temperatures for the fiber materials calcined at 650°C. This is consistent with the increase in Pd particle size and decline in specific surface area as observed as a function of calcination temperature. These results show that for reactions occurring less than 500°C, the Pd/Al₂O₃ fiber materials calcined at 650°C gave the best performance.
Figure 4.16 HRTEM images of Pd/Al$_2$O$_3$ fibers before (A, C) and after (B, D) NO-CO reaction.

Figure 4.16 shows the HRTEM images of Pd/Al$_2$O$_3$ fibers calcined at 650°C before and after NO-CO reaction. First, statistical size analysis (At least 100 measurements) gave an average particle diameter of 5.35 ± 1.51 nm before reaction and 5.01 ± 1.18 nm after reaction. There have been no significant particle size change through the reaction tests, indicating little sintering problem. For other fibers calcined at 750 – 1050°C, any size changes have not been observed in the microscopy study. Furthermore, the stability of Pd nanoparticles were still found with uniform distribution on alumina nanofiber.
4.5 Conclusions

Palladium doped alumina submicron fibers were produced by electrospinning and calcination of the polymer template fibers. These materials were tested for catalytic performance of decomposition of NO and CO gases. The samples were characterized by SEM, TEM, BET, EDX, and XRD.

The average fiber diameter and specific surface areas decreased with calcination temperature. The fiber crystal structure changed from amorphous to gamma phase with increase in calcination temperature. The Pd particle size was observed to significantly increase with the calcination temperature. The reaction data showed the conversion temperature also increased with calcination temperature because the characterization results of Pd/Al₂O₃ nanofibers calcined with an increase temperature was not conductive to the sufficient contact between catalyst on the alumina nanofiber and NO-CO molecules. The fibers calcined at 650°C had the lowest conversion temperature and highest reactivity.
CHAPTER V

PALLADIUM-GOLD NANOPARTICLES SUPPORTED BY TiO$_2$ FIBERS FOR CATALYTIC NO DECOMPOSITION BY CO

5.1 Objectives

The objective in this work is to study the Pd-Au nanoparticles supported by TiO$_2$ fibers. No studies have been reported to date on fiber supported Pd-Au for the NO and CO reaction though Pd-Au alloy catalyst was proven to be superior to single metal catalyst for the hydrogen evolution [163, 164] and CO oxidation [165] reactions.

5.2 Introduction

Nitrogen oxides (NOx) and carbon monoxides (COx) gases are emitted from automobile engines and industrial plants that contribute to atmospheric pollution [166, 167]. Catalyzed reactions are considered the most efficient and cost effective methods to simultaneously eliminate NO and CO pollutant molecules from air [15]. Nano-sized catalyst particles have high surface areas per unit mass that enhances heterogeneous reaction rates. Nanoparticles supported on
electrospun fibers immobilize the particles yet provide high interfacial surface areas for the catalyst particles to contact the reactant gases [4].

Pd, Pt, and Rh doped sub-micron sized alumina fibers have been investigated and applied for manufacture of fibrous porous fiber media to perform NO reaction with metal groups in the presence of CO [49, 168]. Shahreen et al. noted that NO decomposition temperature depends on the anatase phase concentration of Pd doped TiO$_2$ fibers [3].

In this work Pd-Au and Pd composite nanoparticles are dispersed on and within TiO$_2$ submicron sized fibers to form Pd-Au/TiO$_2$, Pd/TiO$_2$ composite fiber structures. These fibers are characterized by SEM, TEM, EDX, XRD, BET and XPS. Reaction performances of the Pd-Au and Pd particles on titania fibers are compared.

5.3 Experiment

This part is going to describe the procedures for the fabrication of the fiber media and catalytic reaction test set up.

5.3.1 Materials

A 16 wt% solution of polyvinylpyrrolidone (PVP, Aldrich, $MW$: 1,300,000) was prepared by dissolving PVP in 10 ml ethanol (AAPER alcohol, 200 proof), 10 ml N,N-dimethylformamide (Fisher Scientific, ≥99.8%), and 10 ml acetone (Sigma-Aldrich, ≥99.5%) and stirred for 12 hours. A titanium isopropoxide solution was
prepared by blending 6 ml titanium isopropoxide (Sigma-Aldrich, 97%), 12 ml acetic acid (Sigma-Aldrich, ≥ 99.7%), and 12 ml ethanol. The PVP and titanium solutions were combined well stirred for 4 hours at room temperature to form the electrospinning solution for synthesizing fibers.

To form fibers with catalyst particles, 86.4 mg (0.49 mmol) of palladium chloride (Pressure Chemical, 60% Pd) and 57.6 mg (0.17 mmol) of gold chloride hydrate (Sigma-Aldrich, 99.999% metal basis) were blended. As well as pure Pd and pure Au particles were synthesized using a similar procedure with different amount of PdCl\textsubscript{2} and HAuCl\textsubscript{4}. The final blended solution contained 2.5 wt% PdCl\textsubscript{2} + HAuCl\textsubscript{4} with respect to titanium isopropoxide. This solution was stirred overnight at 40 °C using a magnetic stirrer.

5.3.2 Preparation of Pd-Au/TiO\textsubscript{2} fibers and catalytic fiber medium

The electrospinning solution was electrospun into PVP fibers containing catalyst and titanium precursors using a laboratory electrospinning setup as depicted in Figure 5.1 and described elsewhere [3, 4]. The detailed explanation of electrospinning experiments have been described in the experiment section of chapter 4.

The collected electrospun fibers were calcined in air at 550°C to remove the polymer and to convert the sol precursor to ceramic form. The PdCl\textsubscript{2} and HAuCl\textsubscript{4} were reduced to metallic form by reaction with hydrazine monohydrate.
The reduction was carried out by immersing the electrospun and calcined PdCl$_2$ + HAuCl$_4$ / TiO$_2$ fiber in the hydrazine monohydrate solution. The treated fibers were separated from the hydrazine solution by filtration, washed using ethanol and vacuum-dried at 80°C for 24 hours to remove the residual solvents.

![Double needle electrospinning setup](image)

Figure 5.1 Schematic diagram of the double-needle electrospinning setup.

The TiO$_2$ fibers containing catalyst particles were fabricated into a high permeability fibrous mat structure by blending the submicron fibers with chopped alumina microfibers into an aqueous slurry and vacuum molding the slurry. Figure 5.2 shows examples of the dry fiber media. The vacuum mold had an inside diameter of 2.3 cm resulting in the fibrous media to have approximately the same 2.3 cm diameter.
Figure 5.2 Fiber media of 2.3 cm diameter formed of alumina microfibers and (A) Pd-Au / TiO$_2$ (B) Pd / TiO$_2$, (C), Au / TiO$_2$, and (D) TiO$_2$ submicron fibers.

5.3.3 Catalytic reaction set up for NO decomposition by CO

The detailed explanation of Pd-Au catalytic fiber media reaction set up have been introduced in the experiment section of chapter 5. The reaction gases consisted of 1 mole/mole % NO, 1% CO, and 98% He, and the inlet volumetric flow rate of 100 sccm. Each experiment was repeated three times with the same inlet flow rates and same inlet concentration ratio of the gases.

The NO and CO conversions were calculated based on the following equations and definitions. The rate of conversion is defined by

\[ X_a = \frac{F_{a,0} - F_a}{F_{a,0}} \]  

where $F_{a,0}$ and $F_a$ are the inlet and outlet molar flow of gas species $a$ (mole/s), respectively. The conversion, $X$ (Eq. 1), is the total number of moles of gas $a$, that reacted per mole of $a$, fed to the reactor.
The disappearance rate \((-r_a^-)\) of NO and CO per mass of catalyst, was calculated using [170]

\[
-r_a^- = \frac{F_{a,0} \cdot X_a}{\Delta W_{cat}} = \frac{C_{a,0} \cdot v_0 \cdot X_a}{\Delta W_{cat}} = \frac{v_0}{RT} \cdot \frac{P_T}{W} \cdot X_a
\]  

(2)

where \(X_a\) is the fractional conversion of gas \(a\), \(\Delta W_{cat}\) is the amount of catalyst (g), \(C_{a,0}\) is the entrance concentration of gas \(a\) (mol/cm\(^3\)), and \(v_0\) is the entrance volumetric flow rate (cm\(^3\)/s).

The inlet concentration, \(C_{a,0}\), can be calculated from the inlet stream temperature and pressure, molar flow rates, and volumetric flow rate via the ideal gas law. The disappearance rate \((-r_a^-)\) of NO and CO was calculated using \((-r_a^- = -r_a^- / S_{metal}\)), where \(S_{metal}\) is the specific surface area of the Pd and Pd-Au nanoparticle catalysts. The turnover frequency (TOF) for NO and CO was calculated by [170]

\[
TOF = \frac{-r_a^- \cdot N_A}{S'}
\]

(3)

where \(N_A\) is Avogadro’s number, and \(S’\) is the surface atom density of Pd-Au nanoparticles.
5.4 Summary and discussion

Figure 5.3(A) shows a sample SEM image and a sample fiber diameter distribution calculated from multiple images of the Pd-Au/TiO$_2$ fibers. The morphologies of the fibers were continuous, smooth and without beads. Fibraquant 1.3 software (nano Scaffold Technologies LLC) was used to interpret the images to determine the fiber size distributions. The fiber diameters were in the range of 30 – 300 nm with an average diameter of 117nm ± 68nm as indicated in Figure 5.3(B). Figure 5.3(C) shows the highlighted region (within the circle) that was evaluated by EDX. The EDX spectra and the elemental compositions of the fibers are listed in the table in Figure 5.3(D). The data show the fibers in that particular sample had 2.63 wt% of Pd-Au metal which is close to the expected 2.5 wt% based on the material compositions of the electrospinning solutions. The atomic molar ratio of Pd : Au = 2.6 : 1 (EDX data) is also a reasonable comparison with the Pd-Au molar ratio of 2.88$^{(Pd)}$ : 1$^{(Au)}$ expected from composition of the electrospinning solution.
Figure 5.3 (A) SEM Image of Pd-Au/TiO$_2$ fibers, (B) Fiber diameter distribution and (C) SEM image with (D) the corresponding EDX analysis of elemental composition of Pd-Au/TiO$_2$ fibers.

Figure 5.4 shows the TEM images and size distribution of catalyst particles in or on the fibers. Figure 5.4 (B) shows a good dispersion of Pd-Au particles within and near the surface of the TiO$_2$ nanofibers. The statistically calculated average particle size was 7 nm with a standard deviation of 3 nm.
Figure 5.4 (A) TEM Image of Pd-Au/TiO$_2$ fibers, (B) magnified view of TEM image, (C) Particle size distribution, (D) HRTEM image of a single Pd-Au particle on a TiO$_2$ fiber, and (E) SAED patterns of Pd-Au/TiO$_2$ fibers.

Figure 5.4 (D and E) were magnified to study the lattice fringe areas and the selected-area electron diffraction (SAED). The HRTEM image in Figure 5.4 (D) shows clear lattice spacing throughout the Pd-Au nanoparticles, suggesting a single crystallinity and alloy formation. However, some of the Pd and Au in the fibers may exist as a distribution of monometallic crystallites or as bimetallic particles. More extensive analysis in future work is needed to determine the full extent of the presence of these compositions.

The crystallinity of the Pd-Au/TiO$_2$ fibers was confirmed by SAED, which revealed two broad diffraction rings corresponding to the (101) for anatase-TiO$_2$ and (111) for Pd-Au particles reflections in Figure 5.4 (E). The relatively faint
unlabeled diffraction rings may be indications of some other crystal structures of the titania component of the Pd-Au/TiO₂ fibers.

Figure 5.5 shows the XRD peaks of Pd-Au/TiO₂ and Pd/TiO₂ fibers after reduction with the hydrazine monohydrate. The characteristic peaks for Pd-Au, marked by the indices (111), and (200), revealed that the resultant particles were essentially face-centered cubic (fcc) structures.

Figure 5.5 XRD diffraction peaks of (upper curve) Au/TiO₂, (center curve) Pd-Au/TiO₂, and (lower curve) Pd/TiO₂ after reduction with hydrazine monohydrate.

For comparison of peaks position among Au/TiO₂, Pd-Au/TiO₂ and Pd/TiO₂, it was also found in the inset of Figure 5.5 that the peak positions slightly shifted toward a lower diffraction angle. The shift in XRD peaks is consistent with an increase of Au content, showing a successful fabrication of some alloyed Pd-Au particles [171, 172].
Figure 5.6 (A) N\textsubscript{2} adsorption-desorption isotherms (Top left inset: BJH pore size distribution curves of Pd-Au/TiO\textsubscript{2} nanofibers).

The surface textural characteristics for Pd-Au nanoparticles supported by TiO\textsubscript{2} nanofibers before and after reduction process were estimated via gas adsorption measurements by studying the adsorption and desorption isotherms with the inset corresponding BJH pore size distribution (Figure 5.6). Both of the samples had similar profiles with classical type IV adsorption model performances [144]. The capillary condensation steps occurred at a relative pressure of about 0.45. In plots in the inset in Figure 5.6 shows the BJH pores had narrow size distributions in the range of 1 to 13 nm. The estimated specific BET surface areas of the Pd-Au/TiO\textsubscript{2} fibers before and after the reduction process were 109 m\textsuperscript{2}/g and 115.2 m\textsuperscript{2}/g respectively with the corresponding BJH average pore diameters of 4.4 nm and 4.9 nm.
To further verify the above analyses, X-ray photoelectron spectroscopy was used to evaluate the chemical bonding before and after reduction with the hydrazine monohydrate. The high resolution XPS spectra corresponding to Pd 3d and Au 4f binding energy regions (330-350 eV and 80-90 eV, respectively) are shown in Figure 5.7. The data were fitted with asymmetric peak shapes after Shirley background correction, assuming the Pd was present in 3 different chemical environments. The Pd 3d spectra before reduction revealed that multiple oxidation states of palladium existed in the samples. The Pd 3d doublet peaks were fitted with the three components corresponding to metallic Pd and oxidized PdO and PdO$_2$. The energies for the 3d$_{5/2}$ peaks were 334.7, 335.9, and 337.8 eV respectively. Further, the data show that after calcination of the electrospun fibers, the PdO and PdO$_2$ spectral peaks were dominant, while a smaller amount of metallic Pd was also present. These values are in good agreement with the reported binding energies [21, 169, 173, 174].
Figure 5.7 XPS peaks of Pd 3d (A) and Au 4f (B) before reduction (lower plots) and after reduction (upper plots).

After reduction using hydrazine monohydrate, the PdO and PdO$_2$ presence was not detected and only palladium metallic peaks were detected at 334.5 and 340 eV, Figure 5.7 (A).

The XPS peaks in the in the 80 to 90 eV range were attributed to Au 4f$^{7/2}$ at 83.0eV and 4f$^{5/2}$ at 86.8eV. As a result of the reduction process, the Au 4f peaks shifted towards lower binding energies by 0.26 and 0.25eV, respectively. In comparison with pure Au XPS peaks (84.0 and 88.0 eV) [175, 176], the shift in binding energy towards the lower energies were more pronounced. The negative
shift of about 1.00eV of the Au 4f peaks from monometallic Au 4f peaks may be due to the addition of Pd to the catalyst particles [59]. Conceivably these shifts in binding energies could be due to the charge transfer from the Pd atoms to the Au atoms, which is indicative of alloy formation [68]. The noticeable negative shift in the Au 4f peak energies observed in our nanofibers could be due to many agglutinations between the Au and Pd atoms in the nano particles in the TiO$_2$ fibers, which increases the opportunity for electron transfer from Pd to Au atoms [62, 177].

To compare the catalytic performance between Pd-Au and Pd particles three different fiber media were tested in the NO+CO reaction. The reaction results are plotted in Figures 5.8 and 5.9.

In Figure 5.8 the outlet stream species concentrations are plotted as a function of the reactor temperature. The inlet compositions for the reactions were essentially the same as the outlet concentrations at 100°C. All of the data points represent the averages of at least three replications and the error bars are one standard deviation of the averaged values. All of the media were the same in thickness and amounts of fibers, and all of the experiments were operated at the same flow rates, hence the relative reactivities of the catalysts corresponded to the reactor temperatures at which the reaction approached completion. The catalysts with higher activities had lower the reactor temperatures at which the CO and NO compositions approached zero.
Figure 5.8 Catalytic performance of (A) Pd-Au/TiO$_2$, (B) Pd/TiO$_2$, (C) Au/TiO$_2$, and (D) TiO$_2$ fiber media.

The Pd-Au/TiO$_2$ fiber media showed the highest catalytic reaction activities [Figure 5.8(A)] where the NO and CO concentrations approached zero at about 250°C reactor temperature. NO – CO concentrations began decreasing at temperatures above 100°C, indicating that the catalyst was active for the NO – CO reaction. As the reaction temperature increased, the NO was converted to nitrogen (N$_2$) and nitrous oxide (N$_2$O). N$_2$O was formed as an intermediate product and underwent further reaction with CO to produce N$_2$ and CO$_2$, as indicated by the
gradual decrease in N\textsubscript{2}O concentrations at higher temperatures. Cho \textit{et al.} and Pisanu \textit{et al.} reported that the formation of N\textsubscript{2}O was a significant intermediate step during the NO – CO reaction [178, 179].

The Pd/TiO\textsubscript{2} (Figure 5.8B) and Au/TiO\textsubscript{2} (Figure 5.8C) fiber media showed similar trends, but the reactions were completed at higher reactor temperatures of about 350°C, indicating lower reaction activities. Thus, the combined Pd-Au catalytic particles had improved performance over the Pd alone and Au alone catalysts. Figure 5.8(D) shows the performance of the TiO\textsubscript{2} fiber media without Pd or Au particles. The NO and CO concentrations approached zero at reactor temperatures above 450°C showing low catalytic activity of the TiO\textsubscript{2} by itself.

As another way of presenting the reaction results, the percent conversions of NO and CO plotted as functions of reactor temperature in Figure 5.9. The plots clearly show the Pd-Au/TiO\textsubscript{2} media had conversions approaching 100% at lower temperatures than the Pd/TiO\textsubscript{2}, Au/TiO\textsubscript{2} and TiO\textsubscript{2} fiber media. The light-off temperatures of 50% NO conversion (T\textsubscript{50}) is another indication of the relative reactivities of the media. The NO T\textsubscript{50} values for Pd-Au/TiO\textsubscript{2}, Pd/TiO\textsubscript{2}, Au/TiO\textsubscript{2} and TiO\textsubscript{2} were 189°, 205°, 258° and 393°C respectively. Similarly, the CO T\textsubscript{50} values were 204°, 239°, 227° and 387°C respectively.
Figure 5.9 Catalytic conversion of NO (%) and CO (%) for catalytic fiber media based on (A) Pd-Au/TiO$_2$, (B) Pd/TiO$_2$, (C) Au/TiO$_2$, and (D) TiO$_2$ fibers only (no added catalyst particles).

The turnover frequencies (TOF) of the NO and CO reaction activity are compared in Figure 5.10. Initially, the Pd-Au/TiO$_2$ fiber medium had the highest TOF values compared to Pd/TiO$_2$ and Au/TiO$_2$ at 150°C. At higher temperatures Au had a higher TOF. These data show the Pd-Au combined particles promoted the NO decomposition reaction kinetics by CO. The TOFs were calculated assuming bimetallic crystallinity of the Pd-Au particles, but as discussed previously, some of the metals may be present as monometallic crystallites or as bimetallic particles. Hence the TOF values are not reliable until more information is available on the crystalline states of the metals.

The activation energies $E_a$ were calculated from the Arrhenius plots (insets of Figure 5.10) for the reaction of NO and CO. The $E_a$ values were 31.5 KJ/mol,
24.2 KJ/mol, and 17.8 KJ/mol for Pd/TiO$_2$, Au/TiO$_2$, and Pd-Au/TiO$_2$ respectively. The reaction kinetic data shows that the activation energy decreased for the combined Pd and Au metals in the TiO$_2$ fibers.

This shows that the addition of Au is beneficial to the catalytic reaction of NO with CO and is consistent with data reported in literature for composition ratios Pd:Au = 4:1 [21, 83]. In support of these observations our results show that the synergetic effect between Pd and Au leads to a higher activity catalyst, thus effectively promoting the decomposition of NO by CO.

Additionally, the catalytic function caused by the incorporation of the larger Au atom into the Pd lattice shifts the d-band center upwards relative to the Fermi level [58, 68]. Therefore, it strengthen the interaction between the gases and the Pd metal surface. At the same time, the ligand effect of Au results in the downshift of the d-band center, thus weakening the binding of adsorbates and metal surfaces, which implies a lower activation energy and an easier reaction than monometallic Pd or Au particles [21, 57, 59, 165]. However, For the Pd-Au catalytic nanoparticle supported on the fiber structure, density functional theory (DFT) calculation should be performed in future work to investigate CO oxidation Pd-Au bimetallic (111) surfaces to gain insights on the catalytic activity of Pd-Au particles.
Figure 5.10. Turnover frequency (TOF) for NO (A) and CO (B) using Pd/TiO$_2$, Au/TiO$_2$, and Pd-Au/TiO$_2$ (Inset: Arrhenius plots for NO and CO).

5.5 Conclusions

This study introduced a practical method for the preparation of fibrous catalytic media based on Pd-Au nanoparticles supported by TiO$_2$ nanofibers. The Pd-Au/TiO$_2$ fibers morphology study was confirmed by SEM, TEM and HRTEM. The crystal structures and chemical states of the Pd-Au/TiO$_2$ fibers were evaluated by XRD and XPS. The reactivities of the Pd-Au combined fiber media were greater than Pd alone and Au alone fiber media. The enhanced reaction activities of Pd-Au/TiO$_2$ fiber media corresponded with decreased activation energies in the Arrhenius expression.
6.1 Objectives

In this work, the different composition of Pd-Au catalysts, as well as pure Pd and pure Au are synthesized by electrospinning method to understand the enhanced CO oxidation activity compared to single metal catalyst. We further report the influence of the presence and content of a second metal (Pd or Au) on the Pd-Au alloy nanoparticle size and dispersion.

6.2 Introduction

Currently, the catalytic oxidation of carbon monoxide is a very convenient and efficient method for processing automotive exhausts and industrial off-gases [180]. Thus, noble metals in the form of nanocrystals which are highly prone to chemisorption of CO and metal oxides with appreciable oxygen vacancy (high oxygen storage capacity) which are best favorable sites for O₂ adsorption provide ideally synergistic condition for CO oxidation [181, 182].
The high activity of supported gold nanoparticles for catalyzing CO oxidation at room temperatures has been well documented over the past 20 years [21, 70]. Recently, Pd-based alloy catalysts have also been investigated to improve catalytic activity [73, 183, 184]. Compared to monometallic Pd nanoparticles, bimetallic systems are more interesting as the increase in the complexity of catalysts offers more possibilities to increase catalytic reactivities. Thus, a better understanding of the Pd-Au bimetallic synergetic effects and the correlation between the surface composition of Pd-Au nanoparticles and catalytic performances should be explored.

Heterogeneous catalysts have been prepared using different preparation methods [22, 75, 163, 165]. Typical preparation methods include deposition of metal nanoparticles on a monolithic support via gas-phase decomposition, in situ growth of metal nanoparticles on colloidal particles or carbon nanotubes via solution-phase reduction, and immobilization of metal nanoparticles onto colloidal particles or electrospun fibers [185-187].

Electrospinning is a very useful technique to immobilize metal nanoparticles on a polymeric or ceramic nanofibers. Pd/Al₂O₃, Pd/TiO₂ and many other catalysts have been prepared using electrospinning[3, 4, 49, 186, 187]. To the best of our knowledge, Pd-Au alloy nanoparticles dispersed on TiO₂ sub micron sized fibers for CO oxidation have not been reported.
6.3 Experiment

This part is going to describe the procedures for the fabrication of the fiber media and catalytic reaction test set up.

6.3.1 Chemicals

Polyvinylpyrrolidone (PVP, \( MW: 1,300,000 \)), acetone (\( \geq 99.5\% \)), titanium isopropoxide (97\%), acetic acid (\( \geq 99.7\% \)), and Gold chloride hydrate (99.999\% metal basis) were purchased from Sigma-Aldrich. Ethanol (200 proof), N, N-dimethylformamide (DMF, \( \geq 99.8\% \)), and Palladium chloride (60\% Pd) were purchased from AAPER alcohol, Fisher Scientific, and Pressure Chemical, respectively. All chemicals were used as received without any further purification.

6.3.2 Synthesis of \( \text{PdCl}_2 - \text{HAuCl}_4 / \text{TiO}_2 + \text{PVP} \) electrospinning solutions

There are four major steps to prepare the catalytic titanium fiber electrospinning solution. These steps involve preparation of polymeric solution, preparation of ceramic precursor solution, mixing of the polymeric and ceramic precursor solutions, and finally addition of catalytic particles precursor to the polymeric-ceramic precursor solution. The polymer solution was used for the electrospinning process.

First, 16 wt.% of PVP solution was prepared by dissolving PVP in a mixture of 10ml ethanol, 10ml DMF, and 10ml acetone. Second, the ceramic precursor
solution was prepared by mixing 6ml titanium isopropoxide, 12ml acetic acid, and 12ml ethanol. Then the polymer solution and the ceramic precursor solution were mixed together to make the electrospinning solution.

Finally, 71.2mg (0.40mmol) of Palladium chloride ($\text{PdCl}_2$) and 68.3mg (0.20mmol) of Gold chloride hydrate ($\text{HAuCl}_4$) were added to the prepared electrospinning solution and stirred overnight at 40 °C using a magnetic stirrer. $\text{Pd}_1\text{Au}_1$, $\text{Pd}_1\text{Au}_2$, $\text{Pd}$, and $\text{Au}$, nanoparticles doped $\text{TiO}_2$ sub micron sized fibers were synthesized using similar procedures with different amounts of $\text{PdCl}_2$ and $\text{HAuCl}_4$, respectively.

6.3.3 Electrospinning, Preparation of fiber media, and Catalytic reaction test

The electrospinning setup, vacuum molding process for making 2.3 cm fiber media, and catalytic reaction test have been reported in the experiment section of chapter 4 and 5. For the carbon monoxide oxidation test, the reaction gases consisted of 1 mole/mole % CO, 1% $\text{O}_2$, and 98% He, and the inlet volumetric flow rate of 100 sccm. Each experiment was repeated three times with the same inlet flow rates and same inlet concentration ratio of the gases.
Figure 6.1 Overall preparation procedures of 2.3cm fibrous fiber media based on catalytic nanoparticles (Au, Pd, or Pd-Au) doped TiO$_2$ submicron sized fiber. Step (A): electrospinning solutions, Step (B): electrospinning, calcination, and reduction of only Au, Pd, or Pd-Au doped TiO$_2$ fibers, and Step (C): Final catalytic media out of catalytic submicron sized titania fibers and Alumina microfibers [(1)Au/TiO$_2$, (2)Pd$_1$Au$_2$/TiO$_2$, (3)Pd$_1$Au$_1$/TiO$_2$, (4)Pd$_2$Au$_1$/TiO$_2$, and (5)Pd/TiO$_2$].

The overall preparation procedures are summarized in Figure 6.1. It shows that the comprehensive procedures for the fibrous fiber medium based on catalytic nanoparticle doped TiO$_2$ submicron consists of three major steps: (A) electrospinning solutions, (B) electrospinning, calcination, and reduction of catalytic TiO$_2$ fiber, and (C) Au, Pd, or Pd-Au alloy structure catalytic particles
doped TiO$_2$ fiber medium. Each fiber medium has a diameter of approximately 2.3cm to be inserted into the reactor that had a hole with a diameter of 2.3cm.

6.4 Summary and discussion

Figure 6.2 shows the morphological images observed by SEM (left column) including fiber size distribution and TEM (right column) images for Pd-Au alloy nanoparticle doped TiO$_2$ fibers. Each distribution of the fiber diameter was measured from at least 10 images. The SEM images of Pd-Au/ TiO$_2$ fibers were prepared by different nanoparticle composition. In Figure 6.2, the fibrous and continuous morphologies electrospun fibers without beads were observed in left column SEM images. The histogram of fiber size distribution show most of the fibers in the size range of 50 - 300nm with the highest frequency (100nm). The average diameters of all fibers were around 110nm as shown in Table 6.1.
Figure 6.2 Fiber size distribution (left column), SEM (middle column), and TEM (right column) images for (A) Au/TiO$_2$, (B) Pd$_1$Au$_2$/TiO$_2$, (C) Pd$_1$Au$_1$/TiO$_2$, (D) Pd$_2$Au$_1$/TiO$_2$, and (E) Pd/TiO$_2$, significant factor ($p = 0.0021$).
The TEM images in Figure 6.2 (right column) present that nanoparticle were well dispersed within and near the surface of the TiO$_2$ fibers, which had a nanoparticle diameter of 19.8nm for Au/TiO$_2$, 14.2nm for Pd$_1$Au$_2$/TiO$_2$, 9.3nm for Pd$_1$Au$_1$/TiO$_2$, 7.2nm for Pd$_2$Au$_1$/TiO$_2$, and 8.5nm for Pd/TiO$_2$, respectively, as shown in Table 6.1. It shows that particle size could be controlled effectively by the addition of amounts of Au. Once the ratio of Pd$_1$Au$_2$ changed to Pd$_2$Au$_1$, the metal particles size became smaller, which agreed well with literatures[25]. Furthermore, the Pd-Au nanoparticles were firmly embedded in the TiO$_2$ nanofibers by electrospinning, calcination, and reduction processes. The monometallic particle Au, Pd, and, alloy structure particle Pd-Au gave a different peak position in the XRD measurements discussed in the next section.

Figure 6.3 SEM-EDX mapping of Pd$_2$Au$_1$/TiO$_2$ fibers.
In order to investigate the elemental quantification analysis, SEM-EDX mapping was performed. SEM mapping images of Pd, Au, Ti, and O elements regarding Pd$_2$Au$_1$/TiO$_2$ fibers, are shown in Figure 6.3. It confirms that Pd and Au nanoparticles were well distributed on the surface of the TiO$_2$ fibers, which corresponds to the particle composition and metal loading data of Table 6.1. Pd-Au particle composition is approximately similar with the ratios of the metal precursors, indicating that reduction of both precursors was successfully carried out after calcination process. The percentage of total metal loading was in range of 4.8-5.3%.

Table 6.1 Fiber size, particle size, composition and metal loading.

<table>
<thead>
<tr>
<th>Material</th>
<th>Fiber size (nm)</th>
<th>Particle size (nm)</th>
<th>Particle composition</th>
<th>Metal loading (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO$_2$</td>
<td>119±53</td>
<td>19.8±1.9</td>
<td>Au</td>
<td>5.3</td>
</tr>
<tr>
<td>Pd$_1$Au$_2$/TiO$_2$</td>
<td>124±57</td>
<td>14.2±1.7</td>
<td>Pd$<em>{35}$Au$</em>{65}$</td>
<td>4.9</td>
</tr>
<tr>
<td>Pd$_1$Au$_1$/TiO$_2$</td>
<td>107±51</td>
<td>9.3±1.1</td>
<td>Pd$<em>{52}$Au$</em>{48}$</td>
<td>4.7</td>
</tr>
<tr>
<td>Pd$_2$Au$_1$/TiO$_2$</td>
<td>99±49</td>
<td>7.2±0.8</td>
<td>Pd$<em>{68}$Au$</em>{32}$</td>
<td>5.0</td>
</tr>
<tr>
<td>Pd/TiO$_2$</td>
<td>105±55</td>
<td>8.5±0.6</td>
<td>Pd</td>
<td>4.8</td>
</tr>
</tbody>
</table>

To further study the comparison before and after reduction process for Pd-Au nanoparticles on the TiO$_2$ fibers, HRTEM images of the two samples were observed in Figure 6.4. Crystalline PdO peaks could not be identified well in HRTEM of Figure 6.4(A). However, very thin amorphous layer was visible at the surface of the particles, suggesting oxide layer on the particles after the calcination process in air.
Figure 6.4 HRTEM images of electrospun Pd$_2$Au$_1$/TiO$_2$ fiber (A) after calcination in air at 550°C for 4 hours (B) after consequent reduction using hydrazine monohydrate, washed and vacuum dried at 80°C (inset: FFT pattern corresponding the particle(B) of HRTEM images).

In Figure 6.4(B), HRTEM image depicts the Pd$_2$Au$_1$/TiO$_2$ fiber after reduction, washed using ethanol, and vacuum-dried at 80°C for 24 hours. And then, this sample transferred into the microscope without contact to air. The results shows that the reduction process led to good single crystallinity with uniform Pd-Au alloy composition and elimination of oxygen atoms from the particle surface.

In addition, the crystallinity of the Pd-Au nanoparticles in Figure 6.4(B) was clearly visible with 0.291nm of lattice fringes, which can be attributed to the Pd-Au(111) planes. These results suggest that uniform single crystallinity of Pd-Au nanoparticles can be generated by electrospinning, calcination, and reduction processes.
The powder X-ray diffraction (XRD) patterns of five different catalyst doped TiO$_2$ fibers are shown in Figure 6.5. The characteristic peaks for Pd-Au, marked by their indices (111), and (200), revealed that the resultant particles were essentially face-centered cubic (fcc) structure. The XRD spectra of the Pd-Au/TiO$_2$ with three different Pd/Au ratios were located between the diffraction peaks of Pd/TiO$_2$ and Au/TiO$_2$, indicating the formation of a Pd-Au alloy. It was also found that the peak positions were slightly shifted to a lower diffraction angle in Figure 6.5(B). The shift in XRD peaks is consistent with an increase of Au content, showing a successful fabrication of the alloyed particles for different Pd/Au ratios.
Figure 6.6 (A) N\textsubscript{2} adsorption-desorption isotherms and (B) BJH pore size distribution curves of Pd-Au/TiO\textsubscript{2} nanofibers.

<table>
<thead>
<tr>
<th>Material</th>
<th>SSA\textsuperscript{a} (m\textsuperscript{2}/g)</th>
<th>Pore diameter\textsuperscript{b} (nm)</th>
<th>Pore width\textsuperscript{c} (nm)</th>
<th>Pore volume\textsuperscript{d} (cm\textsuperscript{3}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO\textsubscript{2}</td>
<td>55.5</td>
<td>5.5</td>
<td>6.1</td>
<td>0.085</td>
</tr>
<tr>
<td>Pd\textsubscript{1}/Au\textsubscript{2}/TiO\textsubscript{2}</td>
<td>72.5</td>
<td>4.3</td>
<td>4.5</td>
<td>0.078</td>
</tr>
<tr>
<td>Pd\textsubscript{1}/Au\textsubscript{1}/TiO\textsubscript{2}</td>
<td>87.6</td>
<td>5.3</td>
<td>6.1</td>
<td>0.134</td>
</tr>
<tr>
<td>Pd\textsubscript{2}/Au\textsubscript{1}/TiO\textsubscript{2}</td>
<td>103.3</td>
<td>4.8</td>
<td>5.2</td>
<td>0.132</td>
</tr>
<tr>
<td>Pd/TiO\textsubscript{2}</td>
<td>115.2</td>
<td>4.9</td>
<td>5.5</td>
<td>0.156</td>
</tr>
</tbody>
</table>

\textsuperscript{a}BET specific surface area, \textsuperscript{b}BJH adsorption average pore diameter, \textsuperscript{c}adsorption average pore width, \textsuperscript{d}BJH adsorption cumulative volume of pores

The surface textural structure property of the fibers was further investigated by BET gas adsorption and desorption study. The N\textsubscript{2} adsorption-desorption isotherms of the prepared Pd-Au/TiO\textsubscript{2}, Au/TiO\textsubscript{2}, and Pd/TiO\textsubscript{2} fibers, exhibited very similar profiles regarding classical type IV performance with a sharp capillary condensation step [144], indicating a well-defined H2 hysteresis loop with a sloping
adsorption branch in the range of 0.4 - 0.9 relative pressure, related to the textural pores between the nanoparticles on the surface of TiO$_2$ fibers (Figure 6.6).

Additionally, the pore size distributions at high pressure were assessed by Barret-Joyner-Halenda (BJH) model according to the adsorption branch as shown in Figure 6.6(B). All samples of pore diameter was observed in the size range of 2-12nm. The corresponding surface area, pore size, and pore volumes of all fibers are summarized in Table 6.2. BET surface area of all samples are between 55 and 115 m$^2$/g. It is interesting to note that the surface area and pore volume increased with an increase of Pd content. These results shows that Pd/Au ratio is an important factor in controlling the final BET surface area and uniformly dispersion of metal components without particle growth (Table 6.1) during the fabrication of Pd-Au doped TiO$_2$ fibers, corresponding well with the above XRD and TEM analysis.

![Graph showing CO conversion (%) of Pd-Au doped TiO2 fiber media.](image)

Figure 6.7 CO conversion (%) of Pd-Au doped TiO2 fiber media.
The catalytic performance of Pd-Au/TiO$_2$ fiber media was evaluated and compared with that of Au/TiO$_2$ and Pd/TiO$_2$ at a fixed flow mixture gases of CO, oxygen, and helium. Figure 6.7 shows that CO oxidation on Au/TiO$_2$, Pd$_1$Au$_2$/TiO$_2$, Pd$_1$Au$_1$/TiO$_2$, Pd$_2$Au$_1$/TiO$_2$, Pd/TiO$_2$ initiated at approximately 150, 175, 125, 100, and 175 °C respectively. Interestingly, under our experimental conditions, the Au/TiO$_2$ fiber media did not show any catalytic activity when reaction temperature lower than 150°C. The possible cause might be size effect of gold particle. In comparison with other studies[188, 189], Au particles size was observed with an approximately 20nm of bulk Au particle size shown in Table 6.1.

With an addition of Pd content, the catalytic activity was changed. Different particle composition of Pd$_1$Au$_2$, and Pd$_1$Au$_1$/TiO$_2$ fiber media with an about 4.8 wt% of metal loading, appeared to increase the catalytic activity temperature from 175°C for Pd$_1$Au$_2$ to 125°C for Pd$_1$Au$_1$. Additionally, the T50 (the temperature required for 50% CO conversion) was 268 and 154°C, respectively. Raising the Pd content of Pd$_2$Au$_1$/TiO$_2$ fiber medium induced a further increase at 100°C of initial activity temperature (T10=125°C, T50=157°C).

Complete (100%) CO conversion occurred at 200°C for Pd$_2$Au$_1$, which indicates a synergetic electronic ligand effect [21, 59]. It should be noted that the Pd$_2$Au$_1$ catalyst doped TiO$_2$ fiber medium was the most active materials compared to other catalyst media.
Figure 6.8 (A) Turnover frequency (TOF) and (B) Arrhenius plots for CO oxidation.

By using the data reported in Figure 6.7 and Table 6.1, the corresponding turnover frequencies (TOF) were calculated in Figure 6.8(A). The Pd$_2$Au$_1$/TiO$_2$ fiber medium gave a TOF values of $1.2 \times 10^{-1}$ s$^{-1}$ at 150°C, indicating significantly higher catalytic activity compared to both $2.5 \times 10^{-6}$ s$^{-1}$ of Pd/TiO$_2$ and $6.9 \times 10^{-5}$ s$^{-1}$ of Au/TiO$_2$ media. Furthermore, the TOF values of Pd$_2$Au$_1$ was about a 5 times higher than that of the Pd$_1$Au$_1$. This data prove that the combined Pd-Au nanoparticle doped TiO$_2$ fiber medium lead to improvement of the CO oxidation kinetics and the catalytic efficiency of Pd-Au alloy systems depends largely on the surface composition of Pd and Au.

Additionally, with increasing the reaction temperature to 250°C, TOF values of Pd$_2$Au$_1$ increased to $2.5 \times 10^{-1}$ s$^{-1}$ at 200°C. Whereas, TOF values of Au/TiO$_2$ was elevated to the highest value of $4.6 \times 10^{-1}$ s$^{-1}$ at 250°C, indicating that all Pd-Au bimetallic and only Pd monometallic nanoparticle doped TiO$_2$ media
became less activity than only Au/TiO$_2$ medium above 250°C reaction temperature.

Figure 6.8(B) shows that the linear Arrhenius plots [ln(TOF) vs 1/T] and the apparent activation energy ($E_a$) of the CO oxidation over the five different Pd-Au particle composition. Interestingly, the activation energy of the Pd$_{1}$Au$_{1}$/TiO$_2$ medium was calculated to be 27.9kJ/mol, which was the lowest value found among the catalyst studied. On the other hand, the steeper slope observed with the mono-metal Pd/TiO$_2$ and Au/TiO$_2$ catalysts corresponds to 84.9, and 61kJ/mol. These similar values are reported in the literatures [59, 165].

In this work, the catalytic activity of Pd–Au/TiO$_2$ fiber media relied significantly on the particle surface composition of Pd and Au. Importantly, the composition of the individual nanoparticles in the catalytic titania submicron-sized fiber could be controlled by varying the percentage of the two metal salts complexed within the fiber medium at the beginning of the electrospinning.

Then, these kinetic study demonstrated that Au considerably enhanced Pd catalytic activity over the composition range Pd:Au=1:1(Pd$_{52}$Au$_{48}$) to Pd:Au=1:2(Pd$_{68}$Au$_{32}$). These enhanced activity of Pd-Au/TiO2 could be attributed to the synergetic effect of Pd with the added Au and highly dispersed active components on the surface of the fibers [25, 60]. In other words, higher metal dispersion means higher exposed metal surface areas and consequently higher catalytic activity. Thus, the combined particle size might have played an important role in the activity profile along with ligand effect(charge transfer between Pd-Au
particles) and ensemble effects (Au prevents Pd aggregation) [21, 60, 68, 70, 165].

The average particle size and particle distribution was found to be 7.2nm and 9.3nm for Pd$_2$Au$_1$ and Pd$_1$Au$_1$, respectively. These two factors could have contributed to the comparatively more activity than mono-metallic Pd/TiO$_2$ and Au/TiO$_2$.

![FTIR spectra](image)

**Figure 6.9** FTIR spectra for CO chemisorbed on Au/TiO$_2$, Pd/TiO$_2$, and Pd-Au/TiO$_2$ fiber media. The samples were outgassed at room temperature after exposure to CO and O$_2$.

The FTIR spectra of absorbed CO were used to identify the surface sites of the Pd-Au/TiO$_2$ fiber media. In Figure 6.9, all appearance of bands indicative of CO in the gas phase was recorded (2169 and 2122 cm$^{-1}$) [190]. For Pd$_2$Au$_1$/TiO$_2$ and Pd$_1$Au$_1$/TiO$_2$ fibers, the bands that appeared at approximately 2082 and 2077 cm$^{-1}$ were assigned to CO absorbed to the Pd-Au alloy structures,
respectively. With increasing the Au content, it contributed to reduce the multi-bonded CO by decreasing the Pd-Au nanoparticle size of the metal ensemble needed for multiple bonding [59, 63, 191] and affect a small transfer of d electrons in the adsorbing palladium through the ligand effect [59, 192]. It could lead to the low frequency shift of the $\text{Pd}_1\text{Au}_2/\text{TiO}_2$ and $\text{Au}/\text{TiO}_2$ fiber materials that appeared at 2045cm$^{-1}$ as shown in Figure 6.9.

6.5 Conclusions

In this work, submicron-sized $\text{Au}/\text{TiO}_2$, $\text{Pd}/\text{TiO}_2$, and $\text{Pd-Au}/\text{TiO}_2$ fiber was prepared by electrospinning, calcination of the polymer template fibers, and hydrazine reduction. The catalytic activity of these materials were tested systematically for CO oxidation. The fiber samples were characterized by SEM, TEM, HRTEM, EDX, XRD, XPS, BET, and FTIR.

The synergetic effect induced by the Pd-Au alloy formation could strongly influence the Pd-Au particle size and catalytic performances. The results revealed that the poor activity for $\text{Au}/\text{TiO}_2$ fiber medium was attributed to the large sizes of the gold particles. However, the decrease of the particle size achieved by the alloy Pd-Au nanoparticles($\text{Pd}_2\text{Au}_1/\text{TiO}_2$ and $\text{Pd}_1\text{Au}_1/\text{TiO}_2$) could avoid the growth of metal particles. In other hands, The catalytic performance was significantly improved in comparison with only $\text{Pd}/\text{TiO}_2$ and $\text{Au}/\text{TiO}_2$ fiber media. Furthermore, the enhanced reaction activity of $\text{Pd}_2\text{Au}_1/\text{TiO}_2$ fiber medium was attributed to a decreased in the activation energy.
CHAPTER VII

COMPARATIVE DISSOLUTION OF ELECTROSPUN Al$_2$O$_3$ NANOFIBERS IN ARTIFICIAL HUMAN LUNG FLUIDS

7.1 Objectives

The concern of fiber persistence in the lung motivates this work to measure the rate of dissolution of the alumina (Al$_2$O$_3$) sub-micron sized fibers. Alumina-based fibers are partially soluble in lung fluids and may not cause pulmonary inflammation [193], which makes them a candidate for development of high aspect ratio nanomaterials that are safe by design.

Unfortunately, little information exists in regard to the physicochemical effects of sub-micron alumina fibers, which include different fiber sizes, surface morphologies, crystal structures, and surface areas with respect to alumina fibers formed by calcination of electrospun polymeric fibers. The aim of this work is to fill in part of the knowledge gap by resolving the influence of these physicochemical properties on the rates that alumina fibers dissolve in artificial lung fluids and evaluate their potential to generate free radicals.
7.2 Introduction

Environmental, health, and safety concerns of nanotechnology have received attention from organizations such as the National Academies [26]. The manufacture, use, and disposal of engineered nanomaterials may lead to exposure of humans to the nanomaterials. Because these materials are relatively new and their biological behavior may differ from that of the bulk material with the same chemical compositions, concerns exist about their potential human health effects. In particular with regard to ceramic nanofibers, there is a paucity of information concerning risk from inhalation exposure.

Recent studies show that physicochemical characteristics of engineered micron and nanomaterials, (size, shape, surface charge, surface area, and composition) can play significant roles in determining their biological response [194-199]. For example, cubic particles with 2μm side lengths and cylindrical particles of 1μm length were internalized by a large fraction of cells, whereas cubic particles with side lengths of 3μm and 5μm were not taken up to any appreciable degree [195]. The shapes of TiO$_2$ nanomaterials were found to influence toxicity, with elongated structures (fibers) having more biological reactivity than short structures or spherical particles of the same chemical composition [197]. ZnO and TiO$_2$ materials with of different shapes, sizes, surface areas, and crystal structures had different cytotoxicity with human lung epithelium cells [198].

From a health and safety perspective fiber materials should be evaluated for their potential to cause pulmonary diseases. In this work, we compared the biodurability of different types of alumina nanofibers in artificial lung fluid models.
and elucidate how the physicochemical properties are controlled by the production process to yield fit-for-purpose nanofibers with varying biodurabilities. Engineering parameters can be manipulated to produce fibers with most favourable biodurabilities within the constraints of the application operating conditions.

7.3 Experiment

This part is going to describe the fabrication of alumina nanofiber and biodurability test set up.

7.3.1 Materials

An aluminium precursor solution was prepared by combining formic acid, aluminium acetate (basic hydrate, (CH$_3$CO$_2$)$_2$AlOH·xH$_2$O, Alfa Aesar), and distilled water at a weight ratio of 1:1:2.5 respectively. This mixture was well stirred. A 9 wt% polymer solution was prepared by dissolving polyvinylpyrrolidone (PVP, Aldrich, $MW$: 1,300,000) in ethanol (AAPER alcohol, 200 proof). The electrospinning solution was prepared by a 1:1 mass ratio of the polymer solution with the aluminium precursor solution for 1 hour at room temperature until completely blended, as indicated when the initially cloudy solution turned clear.
7.3.2 Fabrication of aluminum acetate/PVP composite sub-micron fibers

A porous hollow tube multi-jet electrospinning technique was used to fabricate aluminium acetate/PVP composite fibers [119]. The multiple jet device was composed of a ½ inch PVC pipe with holes, an electrode, a power supply, a grounded collector, and a reservoir as shown in Figure 7.1. The electrode was inserted into the PVC pipe to induce an electric charge into a solution. The electrospinning solution was loaded into the reservoir from which the solution flowed to the pipe. Multiple pendent drops were formed at the holes of the pipe. A voltage potential of about 30 kVDC, high enough to overcome the interfacial tension of the drops [111], was applied to the solution in the pipe to launch the jets towards a grounded collector.

Figure 7.1 Porous hollow tube electrospinning. (A) Schematic diagram. (B) Laboratory setup.

7.3.3 Thermal treatment of electrospun Al$_2$O$_3$ fibers

The electrospun polymer fibers were calcined in air to convert the polymer to ceramic form. The PVP polymer degrades at temperatures higher than 450°C.
In this work, the fibers were calcined using different controlled temperature heating cycles to obtain different crystalline structures: (A) rapid heating to varying soak temperatures (650, 750, 850, 950, 1050, and 1150°C), and (B) different ramp rates (93, 204, 315, and 600°C/hr) to the same soak temperature of 650°C. The soak times were the same for all temperature cycles (4 hr).

Figure 7.2 Temperature profiles of the variations in the heating cycles to calcine the alumina precursor – PVP fibers to fabricate the Al₂O₃ fibers. (A) Variation in
soak temperatures (samples labeled S650 to S1150). (B) Variation in heating ramp rates (samples labeled R93, R204, R315, and R600).

After heating, the samples were allowed to cool slowly in the furnace. The temperature profiles for the various cycles are shown in Figure 7.2. The fiber samples labeled as S650, S750, S850 … S1150 correspond to the different soak temperatures and samples labeled as R93, R204, R315, and R600 correspond to the different ramp rates. As a control, the sample labeled PVP01 corresponds to uncalcined aluminium precursor – PVP fibers. The characterization and dissolution results of the fiber samples are referenced to these labels.

7.3.4 Physical characterization of materials

A high-resolution transmission electron microscope (HR-TEM, FEI Technai F30) operating at 300KV and a Transmission Electron Microscope (TEM, JEM 1200XII) were used to study fiber size and morphology of the Al₂O₃ fibers. Small samples of the fiber mats were cut and placed in acetone, and ultrasonically vibrated to form suspensions. Drops of the suspensions were passed through a carbon coated copper grid, leaving the fibers on the grid for TEM imaging.

Scanning electron microscope (SEM, FEI Quanta 200 at 30kV and HITACHI TM300 at 15kV) images were analyzed to study the fiber morphology and determine fiber size distributions. The diameter distributions were determined from
more than 100 fiber diameter measurements for each sample from the SEM images using FibraQuant 1.3 software (nanoScaffold Technologies LLC).

An X-ray diffractometer (Rigaku D/Max-2000T) with Cu anode (Kα₁ = 0.154056 nm) was used for determination of the crystal phase, crystallinity, and crystal size of the Al₂O₃ fibers. The voltage was set to 40 kV and the current was set to 40 mA. Scans were collected with a step size of 0.1 deg and scan speed of 0.5 deg/min. The crystallite size of alumina fibers was calculated using the Scherrer equation, which relates the full width at half maxima (FWHM), W, of the most intense peak (440) of γ-Al₂O₃ fiber to the angle of incidence, θ, via 
\[ S = \frac{c \lambda}{W \cos \theta} \]
where \( S \) is the average crystallite size, \( c \) is the Scherrer constant and \( \lambda \) is the wavelength. The Scherrer constant can take values from 0.9 to 1.2, depending on the shape of the particles. Here we assumed the spherical shape (\( c = 1 \)).

A Fourier Transform Infrared Spectrometer (Thermo Fisher Scientific Model: Nicolet iS50 FT-IR) was used to determine the molecular bonding information of the samples. The samples were prepared by drying at 75°C for 2 days to completely remove the moisture, and each sample was pressed into discs for the tests. The IR spectra were recorded from 400 to 4000 cm⁻¹ at 8 cm⁻¹ resolution.

The Brunauer, Emmett and Teller (BET) surface areas were measured using nitrogen gas adsorption (ASAP2020, Micromeritics Corp., Norcross, GA). A value of 0.162 nm² was used for the molecular cross-sectional area of N₂ at 77K.
The BET was calculated from at least six adsorption points in the range $p/p_0 = 0.01$ to 0.3; the values were normalized by dry sample mass to calculate specific surface area with units of $m^2/g$.

Powder density was measured using a helium pycnometer (AccuPyc II 1340, Micromeritics) using research grade gas at 15.0 psig. Prior to the density measurements, the fiber samples were placed in an oven at 100 °C to dry overnight and allowed to cool to ambient temperature in a desiccator. A total of 25 consecutive volume measurements were made with the equilibration rate set at 0.0005 psig/min and the results normalized by dry sample mass to calculate density with units of g/cm$^3$.

7.3.5 Artificial lung fluid dissolution studies

The biodurability of the $\text{Al}_2\text{O}_3$ fibers was assessed in two different artificial lung fluid models viz. lung airway epithelial lining fluid having near-neutral pH [200] and alveolar macrophage phagolysosomal fluid having acidic pH [201]. Material dissolution was evaluated using the well-established static technique [202]. With this technique, a known mass of each fiber sample was weighed onto a 0.025-µm pore size 47-mm diameter nitrocellulose filter (Millipore, Bedford, MA) and a second filter of the same type was placed on top to create a ‘sandwich’. The filters served as barriers to particle migration into the dissolution medium which would bias estimates of dissolved alumina. Each filter sandwich was clamped in a dissolution chamber assembly and secured using an o-ring and Teflon screws.
(Figure 7.3) Importantly, the filter pore size (25 nm) was significantly smaller than the diameter of the fibers.

![Diagram of static dissolution chamber assembly with SEM micrograph of S950 material after 7 day exposure to SUF.]

Figure 7.3 Static dissolution chamber assembly; SEM micrograph of S950 material after 7 day exposure to SUF.

The fraction of each fiber sample that was aluminium metal was determined by instrumental neutron activation analysis (Elemental Analysis Inc., Lexington, KY) and used to calculate the initial mass of aluminium from the gravimetrically determined fiber masses. Each filter sandwich was secured tightly in a static dissolution chamber (Intox Products, Moriarity, NM) using four nylon screws and O-rings to provide a particle-tight seal around the edge of the sandwich. Each dissolution chamber assembly was placed in a separate plastic container with 0.080 L of lung fluid and the masses of dissolved aluminium were quantified at pre-designated time points. Triplicate dissolution chambers were prepared for each
Al$_2$O$_3$ fiber. To mimic human lung temperature all samples were maintained at 37 °C for the duration of the respective study periods using a water-jacketed incubator.

To model the fate of particles that deposit in conducting airways, biodurability was evaluated in artificial lung airway epithelial lining fluid termed serum ultrafiltrate (SUF) [200]. Generally, particles that deposit in the conducting airways are bathed in the epithelial lining fluid and cleared by mucociliary action within several hours. Hence, samples of SUF were quantified for dissolved aluminium at 3 hr, 6 hr, 12 hr, 24 hr, 2 day, 4 day, and 7 day (the longer time points were collected to accurately capture the fiber dissolution kinetics). The pH of SUF was maintained at 7.3 ± 0.1 throughout the study by passing flowing CO$_2$ (5%) and air (95%) across the solvent.

To model the fate of particles that deposit in the alveoli, biodurability was evaluated using macrophage phagolysosomal simulant fluid (PSF) [201]. Small particles with aerodynamic diameters below 4 µm can deposit in the distal non-ciliated alveolar (gas exchange) region of the lung. Upon deposition in the alveoli, particles are quickly engulfed by scavenger cells such as macrophages and isolated in vacuoles called lysosomes. The lysosomes merge with phagosomes that contain an acidic milieu to form phagolysosomes that function to sequester and degrade foreign materials over days to weeks. To understand dissolution kinetics over the lifespan of a macrophage cell, masses of dissolved aluminium were quantified following particle immersion for 3 hr, 6 hr, 12 hr, 24 hr, 2 day, 4
day, 7 day, 14 day, 21 day, and 28 day. The pH of PSF was maintained at 4.5 ± 0.1 using 0.02 M potassium hydrogen phthalate buffer.

Analysis of dissolved aluminium was performed using inductively coupled plasma-optical emission spectroscopy without sample digestion. The analytical limit of detection (LOD) for aluminium in SUF was 5µg/L and the limit of quantification (LOQ) was 17µg/L. For PSF, the aluminium LOD was 10µg/L and the LOQ was 43µg/L.

Dissolution rates of the fibers were calculated assuming constant dissolution velocity [203]:

$$k = \frac{2 \cdot \left(1 - \frac{M}{M_0}\right)^{\frac{1}{2}}}{SSA \cdot t}$$  \hspace{1cm} (1)

where \((1-M/M_0)\) is the mass fraction of material dissolved, \(t\) is time (days), SSA is the specific surface area (m²/g), and \(k\) is the chemical dissolution rate constant [g/(m²·day)]. For each material, values of \((1-M/M_0)\) were plotted versus \(t\), and \(k\) was calculated from the slope \((b)\) of the plot for \(t \to 0\) and normalized to \(SSA/2\). The dissolution half-time \(t_{1/2}\) calculated as \(0.693/b\). In general, the dissolution was biphasic and consisted of an initial rapid phase followed by a slower long-term phase. Hence, curves were fitted to the initial and long-term phases separately using a non-linear least squares fitting procedure (SAS 9.2, SAS Institute Inc., Cary, NC). Analysis of variance (ANOVA) F-statistics were used to note overall differences in \(t_{1/2}\) and \(k\) values among materials. When comparing statistical
models that have been fitted to a data set, F-statistic test can be used for identifying the model that best fits the population from which the data were sampled. Tukey’s test was used to identify specific paired differences between means. Tukey’s test should be used on raw data with an ANOVO to find means that are significantly different from each other.

7.4 Summary and discussion

This part is going to explain the alumina fiber characterization and artificial lung fluid dissolution study.

7.4.1 Preliminary study alumina fiber materials

First, two occupationally and experimentally relevant forms of alumina small nano-fibers were selected for measuring their aerodynamic diameter size classification by using the suggested mathematical formulae in Chapter 2.

Figure 7.4 (A,B) Scanning electron microscopy (SEM) images of Al₂O₃ fibers.
The aerodynamic diameter of fibers was determined by measured diameter and length of fibers in SEM images such as Figure 7.4 (A) and (B). After the images were taken, the fiber diameter and length was determined by using ImageJ to calculate the aerodynamic diameter. 100 fibers were chosen to measure the fiber dimensions for each distribution from at least 10 SEM images.

Figure 7.5 Gaussian normal distribution of fiber aerodynamic diameter at different gap distance and pore sizes (A) curve for 0.2mm hole sizes (B) curve for 20cm gap distance.

Figure 7.5 indicates that the aerodynamic diameters were in a range of 1-10μm. Most aerodynamic diameter distributions located on 1-6μm. That curve in Figure 7.5 shows 80% for Dₐ values between 1μm and 5μm. Lung deposition of inhaled fibers is the most efficient in humans for nose breathing when fibers have an aerodynamic diameter less than 3μm [108]. This range can cause adverse
effect in our body. On the contrary to this, as Morgan et al. stated, fibers with $D_a < 1\mu m$ travel back out from the human lower lung with exhaled air [92]. Deposition efficiency decreases to zero when aerodynamic diameter increases to about $6\mu m$ for rats and $8\mu m$ for humans. Inhaled fibers with aerodynamic diameters $> 5\mu m$ are quickly cleared to the throat by the mucociliary escalator [87, 92, 108].

The unique aspect of our study design was that the correlations between dissolution and physicochemical properties of $\text{Al}_2\text{O}_3$ fibers were determined by changes in the fiber size, crystallite size, phase transformation, crystallinity, and specific surface area. These changes are important for understanding nanomaterial dissolution behavior. Depending on the various characteristics of alumina fibers from the variations in the thermal treatments, the dissolution rates and toxicity will change.

7.4.2 $\text{Al}_2\text{O}_3$ fiber characterization

For the analyses of the $\text{Al}_2\text{O}_3$ fibers calcined at soak temperatures $650^\circ\text{C}$, $750^\circ\text{C}$, $850^\circ\text{C}$, and $950^\circ\text{C}$ for 4 hr, the diameters of $\text{Al}_2\text{O}_3$ fibers gradually decreased with increase in the calcination temperature as indicated in Figure 7.6. Figure 7.7 shows the different ramp rates did not have a significant effect on the fiber diameters.
Figure 7.6 (A) SEM, (B) TEM, and (C) length weighted frequency distribution of fiber size of the uncalcined fibers and the fibers calcined for 4 hr at different temperatures, significant factor ($p = 0.0012$).
All of the calcined fibers had diameters smaller than the precalcined PVP polymer fibers due to evaporation of residual solvent and the degradation of the polymer. SEM and TEM images and the corresponding fiber diameter frequency distributions of the uncalcined fibers and the fibers calcined at different temperatures are shown in Figure 7.6.
Figure 7.7 (A) SEM, (B) TEM, and (C) fiber diameter distributions of Al$_2$O$_3$ fibers calcined at 650°C for 4 hr R93(93°C/hr), R204(204°C/hr), R316(316°C/hr), and R600(600°C/hr), significant factor ($p = 0.0001$).

Each distribution of the fiber diameters was measured from at least 10 SEM images. Each histogram was generated out of 500 measurements. It is evident from the distribution plots that the distribution became narrower with calcinations.
at higher temperature. The S950 samples had the lowest average fiber diameter and the narrowest diameter distribution among all the materials. This trend showed that different calcination temperatures directly affected the diameters of the fibers, and is consistent with observations reported in literature [4].

The TEM images in Figure 7.6 show the fibers with higher calcination temperatures appear to have produced a rougher surface morphology. The morphology of fibers calcined at 650 - 950°C, visually changed from smooth surface (S650) to rough surface (S950) in Figure 7.6. The apparent roughness corresponds to the increase in crystallinity of the alumina at the higher temperatures. The changes in surface structural features can be attributed to a difference in crystal formation and transformations from amorphous to γ-phase of alumina fibers (described below).

The SEM, TEM and fiber diameter distributions for R93 – R600 are shown in Figure 7.7. Increasing the temperature ramp rate from 93°C/hour to 600°C/hour appears to not have significantly changed the amorphous nature of the fibers. The smooth fiber surface shown in Figure 7.7(B) indicated that there was not an obvious phase change to a crystalline structure among these samples (R93 – R600) with different heating rate. The average fiber diameters were about the same and the distributions had about the same standard deviations.

To confirm the change of the crystal structure with calcination and to correlate with the observed microscopy data, X-ray diffraction analyses were undertaken. Figure 7.8 shows no crystalline peak on the samples before
calcinations (PVP01) and the fiber samples calcined at soak temperature 650°C (i.e. samples S650 and the fibers calcined at the various ramp rates R93 - R600).

Figure 7.8 XRD Patterns and crystallinity of Al$_2$O$_3$ fibers calcined at different soak temperatures and ramp rates.

The XRD patterns of samples with calcination temperatures of 750°C and greater (S750 – S950) showed γ-phase peaks at 2θ = 32.8°, 37.6°, 39.6°, 45.9°, 61.1°, and 67.2° representing the indices of (220), (110), (222), (400), (511), and (440) crystal planes of Al$_2$O$_3$. The crystallinity of the samples increased with the
soak temperature from 13.2% to 40.6% with 8nm crystallite size of γ-Al₂O₃ fibers as displayed in Figure 7.8.

![Figure 7.9 Specific surface area of Alumina fibers. (A) PVP01, (B) fibers rapidly heated to final soak temperatures (S650-S1150); (C) fibers heated at different ramp rates to soak temperature 650°C(R93-R600).](image)

Figure 7.9 shows the specific surface areas for all of the samples. The specific surface areas increased up to soak temperature 850°C followed by a decrease in area at soak temperature 950°C. To determine if the decline in surface area continued at higher temperatures, additional samples were calcined at temperatures 1050 and 1150°C (S1050 and S1150). The surface areas of the additional samples plateaued at about 16 g/m². Samples calcined at the different ramp rates to the same soak temperature (R93-R600) did not show significant
change in the specific surface area, indicating the soak temperature is the more important factor.

BET and XRD characterization were performed to comprehend the correlation between the reduction of surface area and crystal structure. Generally, during the transition from γ- to α- Al₂O₃ crystal phases, a dramatic reduction in surface area occurs [121, 145]. Upon heating, the γ-Al₂O₃ goes through a series of transformations to reach the thermodynamically stable α-Al₂O₃ phase structure [31, 122, 145]. Thus, the surface grain coarsening of the Al₂O₃ fiber incurred during calcination can lead to reduction of the specific surface area [31].

![Figure 7.10 XRD Plots of alumina fibers calcined at 650 – 1150 °C.](image)
Figure 7.10 shows that alumina fibers calcined at 1050°C (S1050) and 1150°C (S1150) had alpha crystal structures with 15nm and 17nm of estimated crystallite sizes. The increase in peak intensities with increase in temperature shows the progressive increase in the alpha phase content of the fibers and the coalescence of the tiny crystallites started accelerating the grain growth to go to alpha phase. From XRD and TEM studies, crystallite growth was also demonstrated by the increase of calcination temperature, which may reveal how phase transformation modified the fiber morphology and crystal structure.

![Graph showing Al content and density of Alumina fiber](image)

Figure 7.11 Al Content(Top) and Density of Alumina fiber(Bottom) (A) PVP01, (B) S650-S950, and (C) R93- R600.

Figure 7.11 shows the atomic alumina content and fiber intrinsic density of the fibers. Within the error of the measurements (relative standard deviation = 6%), the Al content of S950, R204, and R315 matched the value expected from
stoichiometry of Al₂O₃ (52.9%). The calcination temperature clearly made a difference in Al content from PVP01 to S950 in Figure 7.11(top). However, regardless of ramp rate, samples R93 to R315 had similar (but slightly less than theoretical) Al content apart from R600 samples. Al content of R600 was approximately 40%. In Figure 7.11(bottom), the density of the samples also increased with calcination temperature, which was also related to agglomerated grains on the surface of the alumina fibers calcined at high temperature. Density of R93, R204… R600 samples having different ramping rate had no significant change of the values.

7.4.3 Artificial lung fluid dissolution studies

On a mass basis, the total amounts of aluminium dissolved from the fibers ranged from 0.2 to 13.5% in SUF (Table 7.1) and from 0.5 to 36% in PSF (Table 7.2). In both lung fluid models, the largest total masses of dissolved aluminium were from the uncalcined PVP01 material, which reflects the greater solubility of the precursor aluminium acetate relative to the heat-treated alumina fibers.

Aluminium dissolution was tested in the two types of lung fluid models. Estimates of the dissolution half-time, t₁/₂ (the time to clear half the mass via solubilization) and the chemical dissolution rate constant (k) for the initial rapid phase and latter long-term phase of each Al₂O₃ fiber are summarized in Table 7.1 (SUF) and in Table 7.2 (PSF). In both SUF and PSF, k values for PVP01 were significantly faster than all of the alumina fibers (p < 0.05).
Inhaled alumina fibers that deposit in the conducting airways will be subject to clearance via chemical dissolution and mechanical action (mucociliary-mediated transport). Particle clearance by chemical dissolution depends upon the composition of the airway lining fluid, chemistry of the particle, etc. In contrast, mechanical clearance is independent of these factors and transport to the pharynx (where the particles are swallowed and excreted via the gastrointestinal tract) occurs at rapid rates with half-times of approximately 2 to 8 hr [99]. Hence, for SUF, the calculated $t_{1/2}$ and $k$ values indicate that if Al$_2$O$_3$ fibers deposit in the conducting airways of the lung, little material will dissolve prior to removal by mechanical action.

Once deposited in the non-ciliated alveolar (gas exchange) region of the lung, particles are rapidly engulfed by AM and sequestered within phagolysosomes. The engulfed particles are cleared via chemical dissolution in the acidic microenvironment of the phagolysosomes and by movement of particle-laden cells to the ciliated bronchioles [110], and eventually to the pharynx. Movement of AM to the ciliated bronchioles is a very slow process with half-times of approximately 35 to 7000 days [99].

Generally, the initial and latter phase dissolution half-times of the alumina fibers in PSF were less than 7000 days. The greater solubility of alumina fibers in PSF relative to macrophage-mediated clearance indicates that chemical dissolution is an important clearance mechanism if these fibers were to deposit in the alveoli.
Table 7.1. Dissolution parameters of alumina fibers in SUF (pH 7.4)

Dissolution parameters (Mean ± Standard Deviation)

<table>
<thead>
<tr>
<th>Material</th>
<th>Dissolved (%)</th>
<th>$t_{1/2}$ (days)</th>
<th>$k$ [(g/(cm$^2$·day)]</th>
<th>$t_{1/2}$ (days)</th>
<th>$k$ [(g/(cm$^2$·day)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP01</td>
<td>13.48±6.66</td>
<td>9±3</td>
<td>5.6±2.0 x 10^{-5}</td>
<td>125±57</td>
<td>4.4±2.3 x 10^{-6}</td>
</tr>
<tr>
<td>S650</td>
<td>1.13±0.07</td>
<td>1032±484</td>
<td>1.5±0.7 x 10^{-8}</td>
<td>1764±185</td>
<td>7.5±0.8 x 10^{-9}</td>
</tr>
<tr>
<td>S750</td>
<td>0.56±0.13</td>
<td>1343±385</td>
<td>4.8±1.6 x 10^{-10}</td>
<td>3480±520</td>
<td>1.8±0.3 x 10^{-10}</td>
</tr>
<tr>
<td>S850</td>
<td>0.36±0.11</td>
<td>1689±195</td>
<td>2.9±0.3 x 10^{-10}</td>
<td>5515±1223</td>
<td>1.0±0.0 x 10^{-10}</td>
</tr>
<tr>
<td>S950</td>
<td>0.22±0.07</td>
<td>4761±2573</td>
<td>3.9±1.9 x 10^{-10}</td>
<td>9881±3394</td>
<td>1.7±0.7 x 10^{-10}</td>
</tr>
<tr>
<td>R93</td>
<td>0.29±0.10</td>
<td>4058±1553</td>
<td>2.1±0.7 x 10^{-9}</td>
<td>6998±2461</td>
<td>1.2±0.4 x 10^{-9}</td>
</tr>
<tr>
<td>R204</td>
<td>0.30±0.03</td>
<td>5874±852</td>
<td>1.2±0.2 x 10^{-9}</td>
<td>5387±1080</td>
<td>1.4±0.3 x 10^{-9}</td>
</tr>
<tr>
<td>R315</td>
<td>0.49±0.13</td>
<td>4933±1880</td>
<td>1.9±0.6 x 10^{-9}</td>
<td>4164±1009</td>
<td>2.1±0.5 x 10^{-9}</td>
</tr>
<tr>
<td>R600</td>
<td>1.13±0.07</td>
<td>1032±484</td>
<td>1.5±0.7 x 10^{-8}</td>
<td>1764±185</td>
<td>7.5±0.8 x 10^{-9}</td>
</tr>
</tbody>
</table>

Table 7.2. Dissolution parameters of alumina fibers in PSF (pH 4.5)

Dissolution parameters (Mean ± Standard Deviation)

<table>
<thead>
<tr>
<th>Material</th>
<th>Dissolved (%)</th>
<th>$t_{1/2}$ (days)</th>
<th>$k$ [(g/(cm$^2$·day)]</th>
<th>$t_{1/2}$ (days)</th>
<th>$k$ [(g/(cm$^2$·day)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP01</td>
<td>35.93±4.05</td>
<td>13±2</td>
<td>3.7±0.6 x 10^{-5}</td>
<td>147±18</td>
<td>3.2±0.4 x 10^{-6}</td>
</tr>
<tr>
<td>S650</td>
<td>3.29±0.47</td>
<td>337±36</td>
<td>3.9±0.4 x 10^{-8}</td>
<td>1958±302</td>
<td>6.8±1.0 x 10^{-9}</td>
</tr>
<tr>
<td>S750</td>
<td>2.16±0.13</td>
<td>390±50</td>
<td>1.6±0.2 x 10^{-9}</td>
<td>2897±201</td>
<td>2.1±0.1 x 10^{-10}</td>
</tr>
<tr>
<td>S850</td>
<td>2.08±0.69</td>
<td>493±221</td>
<td>1.1±0.5 x 10^{-9}</td>
<td>3215±1004</td>
<td>1.6±0.6 x 10^{-10}</td>
</tr>
<tr>
<td>S950</td>
<td>1.18±0.18</td>
<td>925±328</td>
<td>1.8±0.6 x 10^{-9}</td>
<td>5496±961</td>
<td>2.9±0.5 x 10^{-10}</td>
</tr>
<tr>
<td>R93</td>
<td>0.47±0.15</td>
<td>4330±2443</td>
<td>2.3±1.4 x 10^{-9}</td>
<td>16365±5639</td>
<td>5.3±2.0 x 10^{-10}</td>
</tr>
<tr>
<td>R204</td>
<td>0.48±0.20</td>
<td>4294±1119</td>
<td>1.8±0.5 x 10^{-9}</td>
<td>16943±8692</td>
<td>4.9±2.0 x 10^{-10}</td>
</tr>
<tr>
<td>R315</td>
<td>0.47±0.13</td>
<td>3658±99</td>
<td>2.3±0.1 x 10^{-9}</td>
<td>15609±4110</td>
<td>5.7±1.4 x 10^{-10}</td>
</tr>
<tr>
<td>R600</td>
<td>3.29±0.47</td>
<td>337±36</td>
<td>3.9±0.4 x 10^{-8}</td>
<td>1958±302</td>
<td>6.8±1.0 x 10^{-9}</td>
</tr>
</tbody>
</table>

*S650 = S650 is the same experiments with R600
The exception to this observation was the latter-phase dissolution half-times for R93, R204, and R315 which were a factor of two longer than expected for mechanical clearance and would be expected to have prolonged persistence in the alveoli. The slow dissolution and potential persistence of aluminium oxide fibers in the lung alveoli has important implications for understanding human health. Released ions can bind to proteins such as albumin and/or be eliminated through urine. Persistence of particulate can induce pulmonary damage as a consequence of accumulation of non-reactive particles [204]. Aluminium is ubiquitous in our environment and is present in trace amounts in the human body, as such, inhalation and dissolution of aluminium particulate could lead to biomagnification of levels in the body and alter homeostasis.

There were slight increase in the initial rapid or latter long-term dissolution rates among S650(650°C), S750(750°C), S850(850°C), and S950(950°C) in either SUF or PSF. This data is consistent with observations reported in literature [198]. The relatively larger surface area of fibers can induce greater production of reactive oxygen species (ROS), which then can damage of DNA because the ability of nano-sized fibers to trigger generation of reactive oxygen species (ROS) is greater than that of larger micro-sized fibers in biological systems [198, 205, 206]. Thus, this fiber size differential (S650-S950) with respect to ROS generation and toxicity may be explained by the significant increase in the surface area and therefore surface reactivity of the nano-sized fibers.
Next, we evaluated the influence of calcination ramp rate on dissolution using the fibers that were calcined at the same temperature (650°C) but using heating ramp rates of 93(R93), 204(R204), 315(R315) or 600(R600)°C/hour.

The dissolution clearance half-time of R600 was significantly shorter compared to R93, R204, and R315 (p< 0.05). The long term dissolution rates of aluminium from R600 were a factor of five faster in SUF and a factor of 14 faster in PSF relative to R93 – R315, though differences were not significant. These data suggest an effect of calcination ramp rate on dissolution (all four types had similar diameters and densities and were amorphous). Specifically, a rapid ramp rate (600°C/hour) to 650°C yielded a less persistent alumina fiber. For a metallurgical study regarding the effect of ramp rate, some authors showed that densification and fine grain sizes of alumina materials could be changed [207-209].
Figure 7.12. Scanning electron micrograph of alumina fiber S950(950°C) illustrating transverse fiber breakage (see arrows) after exposure to PSF for 28 days. Scalebar = 1 µm.

There have been conflicting results. Stanciu et al. and Zhou et al. reported that the grain size of alumina decreased with increasing heating rate under 45 MPa pressure and high densities was obtained in alumina ceramic materials without any additives [207, 208]. Whereas, Kim et al. stated that the grain size and residual porosity decreased with slow heating rate [209]. Hence, heating ramp rate might affect dissolution results due to the change of the densification and the direct grain to grain contact at molecular scale in alumina ceramic fiber. To fully understand the effect of the ramping rate, additional work should be needed.

Previously, Adamcakova-Dodd et al. evaluated the dissolution of a commercially available Al₂O₃ fiber material using a model of airway epithelial lining fluid and a model of macrophage lysosomal fluid analogous to SUF and PSF,
respectively [193]. Though sold as Al₂O₃ powder, characterization of the as-received material revealed that it was primarily composed of crystalline aluminium hydroxide. The authors reported that the dissolution of aluminium hydroxide was generally linear in both lung fluid models. From their data, we estimated that \( k = 9 \times 10^{-10}\) g/(cm²·d) in their airway lining fluid model and \( k = 4 \times 10^{-9}\) g/(cm²·d) in their macrophage lysosomal fluid. Our \( k\) value estimates for the long-term dissolution of amorphous (with the exception of PVP01, S650, and R600) and crystalline alumina fibers were similar to that derived for aluminium hydroxide.

Visual inspection of Al₂O₃ fibers after 28 days of exposure to PSF indicated that these materials were susceptible to transverse breakage (Figure 7.12). For macrophages to be effective in removing fibers from the alveoli, the fibers should be completely engulfed by the cells. If the fibers are too long, mechanical clearance via particle-laden macrophage migration from the alveoli is less effective. Our observation that the Al₂O₃ fibers break transversely from exposure to PSF is important because breakage transforms long fibers into shorter fibers which are more easily cleared by AMs via migration from the alveoli [105].

7.5 Conclusions

The present study concluded the biodurability of eight electrospun alumina fiber modified by different heating protocol in artificial lung fluid models. We found that first, uncalcined PVP-Al₂O₃ fiber (PVP01) was significantly faster than all other alumina fibers, and alumina fibers calcined from 650°C to 950°C (S650-S950) did
not cause the change of dissolution half-time significantly. Thus, the physicochemical property of Al₂O₃ fiber had no effect on dissolution behavior in either SUF or PSF. For the variation in heating ramp rate (R93-R600), the alumina fibers from R600 had a significantly greater dissolution rate compared to slowly heated alumina fiber samples (R93-R315) even though these four samples had similar physicochemical property such as, fiber diameter, crystal structure (amorphous), surface area, and density. The fibers with increased solubility have a reduced inflammogenic potential. To fully understand the effect of the ramping rate, additional work is needed.

7.6 Acknowledgement of prior publication of the work described

The contents of this chapter were published in reference [135]. The journal allows the paper to be republished as part of a thesis according to their website [210]. A.B.Stefaniak characterized the alumina fibers and evaluated their biodurability, N.Stojilovic performed and interpreted the XRD measurements. A.B. Stefaniak wishes to acknowledge M.G. Duling and R.B. Lawrence for their technical support with the dissolution studies and Dr. M.A. Virji for guidance on statistics. Mention of a specific product or company does not constitute endorsement by the Centers for Disease Control and Prevention. The findings and conclusions in this report are those of the authors and do not necessarily represent the views of NIOSH. N.Stojilovic was supported by UWO FDR859 grant.
CHAPTER VIII

VERTICAL ROD METHOD FOR ELECTROSPINNING POLYMER FIBERS

8.1 Objectives

In this work a unique and relatively simple method to launch multiple jets from a vertical threaded rod is described. The rods were applied individually and in a linear array of multiple rods.

8.2 Introduction

The electrospinning process is a convenient method for producing sub-micron polymer fibers. A voltage potential on the order of 20 kV is applied to a droplet of polymer solution. When the electrical forces within the droplet exceed the surface tension forces, a charged liquid jet launches from the droplet and generally follows the gradient in the voltage potential. The mechanism of electrospinning is well described in literature [117, 118]. Typically the solvent in the polymer solution evaporates and the jet solidifies in a solid fiber with diameter in the submicron to micron size range.
Sub-micron sized fibers have large surface to volume ratios that are useful in many applications such as filtration [3, 211-214]. One of the perceived drawbacks of the electrospinning method for industrial applications is its low production rate. The production rate is limited by the rate at which solution is carried by a single jet [115]. To increase the production rate, multiple jets are needed, but the generation of multiple jets by replicating nozzles significantly increases the capital costs of the equipment. To economically increase the production rate, needless electro-spinning methods have been developed.

Yarin et al. [215] induced the formation of vertical spikes on the flat surface of a polymer solution using a magnetic field from which multiple jets launched. Dosunmu et al. [216] used a porous walled cylindrical tube to distribute multiple drops on the tube surface from which multiple jets launched. Varabhas et al. applied a variation of the porous walled tube by drilling an array of small holes in the wall of a PVC pipe [119]. Commercial equipment have been produced that launch multiple jets from the surface of horizontal solid cylinders, wires, and comb-like structures [217]. Other commercial methods for producing submicron fibers have been developed but are not discussed here.

In most applications the electrospinning jets inherently travel from the charged droplet towards a grounded collector. The collector may be a flat surface to collect the jets to travelling in one predominant direction or it may be a curved surface that wraps around a nozzle so as to collect the fibers that may be launched in many directions. In a few studies the electrical field was modified using secondary electrodes to direct the jets in a specific direction [112, 218, 219].
8.3 Experiment

This part is going to describe the solution preparation, electrospinning setup, and fiber characterization.

8.3.1 Solution preparation

A 6wt% solution of Polyvinylpyrrolidone (PVP, Aldrich, $MW: 1,300,000$) was prepared by dissolving PVP in ethanol (AAPER alcohol, 200 proof). The solution was mixed using a magnetic stirrer for 24 hours at room temperature to completely dissolve PVP particles.

8.3.2 Electrospinning preparation

The electrospinning performances of vertical threaded rods are compared to the performance of a single-needle setup. Figure 8.1 shows a common custom-made single-needle laboratory electrospinning setup. A syringe and tube delivered the polymer solution to a droplet at the tip of a charged metallic needle from which a jet launched [111]. A grounded rotating cylindrical drum collected the fibers with its surface positioned 20 cm from the tip of the needle. The needle was electrically charged to 25kV by a copper wire connected to a high voltage power supply (Gama high voltage, Ormond Beach, FL).
Figure 8.1 Single needle electrospinning. (A) Schematic diagram and (B) Photograph of custom made laboratory setup.

Figure 8.2 shows a single vertical rod electrospinning setup. Droplets or liquid film of the polymer solution flowed downward along the surface of the rod. As the droplets moved many jets launch from the droplets. The jets were collected on a cylindrical collector positioned coaxially to the vertical rod with a gap distance of 20 cm between the collector and the rod. In this work the rod was a common ¼ inch -20 threaded steel rod (6.4 mm diameter, 20 threads per 25.4 mm length, and 50 cm in length). A half-inch Polyvinylchloride (PVC) pipe was used as the horizontal pipe (21.3 mm OD) from which the polymer solution flowed onto the vertical rod. The threads on the surface of the rod provided a surface roughness that caused the liquid surface to undulate. Many of the jets of polymer solution launched from the peaks in the undulations.
Figure 8.2 (B and C) show details of the connection between the vertical threaded rod and the PVC pipe. The rod was threaded through a hole in the bottom side of the wall of the (PVC) pipe. A rubber stopper was used to hold the top of the rod as it protruded through the top side of the PVC pipe. The polymer solution was loaded into the PVC pipe from a pressurized reservoir. The solution flowed through small grooves machined axially into the surface of the rod where it protruded through the hole in the PVC pipe. The rod was electrically charged through a copper wire to 35 kV and jets launch from multiple points along the rod axis.

To study the performance of multiple rods, the rods were arranged in linear arrays of two, four, and five rods to compare the production rates and fiber diameter distributions. Secondary electrodes were positioned on one side of the array to direct the jets toward a planar collector surface. With some experimentation it was found that the applied voltage needed to be increased as the number of rods increased to obtain the best production rates of fibers. The applied voltages were 50kV for 2 rods, 80kV for 4 rods, and 100kV for 5 rods.
Figure 8.2 Single vertical threaded rod electrospinning setup. (A) Schematic diagram of the setup with a coaxial cylindrical collector, horizontal PVC pipe to hold the rod, and reservoir to feed polymer solution to the PVC pipe. (B) Top view of end of threaded rod through an enlarged hole in the top surface of the PVC pipe; arrows point to grooves machined into the surface of the threaded rod to allow flow of polymer solution. (C) Side view drawing of the section of the PVC pipe with the threaded rod protruding from the bottom of the pipe wall and a rubber stopper plugging the larger hole in the top side of the PVC pipe; the threaded rod extended through a hole in the rubber stopper.

The arrays of multiple rods were fabricated similar to the single rod in Figure 8.2 by suspending the multiple rods from a single vertical PVC pipe. Alumina foil as the secondary electrode was attached to a fiberboard and positioned on one side with the surface parallel to the array of rods and along the two ends of the array (as described later). The secondary electrode was charged to about 60 to 80% of the potential charged to the threaded rods to direct the jets.
toward the flat collector. The collector surface, also aluminum foil similarly attached to fiberboard, was electrically grounded. An array with two rods is shown in Figure 8.3.

Figure 8.3 Array with two vertical rods. The arrows show the general directions of the jets. (A) Schematic diagram. (B) Side view. (C) Photograph of the laboratory setup.

The flow rates of the polymer solutions were controlled by raising or lowering the reservoir that increased or decreased the pressure head of the polymer solution. If the flow rate was too slow the drops evaporated and solidified on the rod surface part way down the rod and the number of jets was significantly reduced. If the flow rate was too large the polymer solution flowed as a continuous fluid film that also had a reduced number of jets and hence reduced production rate. The flow rates were adjusted by the operator to obtain the apparent maximum
production rates from the rods. Future study should be conducted on the effect of flow rate on fiber production.

8.3.3 Characterization

Images of fiber mats taken with a scanning electron microscope (SEM) (FEI Quanta 200 at 30kV and HITACHI TM300 at 15kV) were analyzed to study the fiber morphology and to determine the distribution of the fibers diameters. The diameters of the fibers were measured from the SEM images using FibraQuant 1.3 software (nanoScaffold Technologies LLC). Four fiber sheets produced by each configuration were measured for fiber size distributions. In each fiber sheet, 6 SEM images of fibers were taken from samples at six locations of the collector (2 near the top, 2 in the middle, and 2 near the bottom of the collector). The FibraQuant software measures diameters at hundreds of points in a typical image at multiple locations on multiple fibers. The resulting fiber diameter distribution is equivalent to a length-weighted size distribution.

As an aid to the positioning of the secondary electrodes, the electric field lines were modeled using a finite element software (FlexPDE™, PDE Solutions Inc.). The model calculations are useful to visualize how the secondary electrode aids in directing the electric field lines toward the collector and reduce fiber loss to the surroundings. A more systematic parametric study should done both in the aspects of modeling and experiment to predict an ideal rod design in future work.
Gauss's law, or the conservation of charge\cite{120}, was used to model the current density vector, \( j \), for a static electric system in a continuum by setting the gradient of the current density to zero

\[
\nabla \cdot j = 0
\]

\( (1) \)

The electrical conductivity relates the current density to the potential gradient as

\[
j = -\sigma \nabla \phi \]

\( (2) \)

Where \( \phi \) is the electric potential (voltage) and \( \sigma \) is the conductivity of the medium. For a constant conductivity, Eq. (1) and (2) combine to the form of Laplace’s equation in the potential

\[
\nabla^2 \phi = 0
\]

\( (3) \)

The potential field and the current density vector were calculated and plotted in 2- dimensional Cartesian coordinates. Hence Eq. (3) becomes

\[
\frac{\partial^2 \phi}{\partial^2 x} + \frac{\partial^2 \phi}{\partial^2 y} = 0
\]

\( (4) \)

Using the FlexPDE\textsuperscript{TM} software Eq.(4) was solved and plotted to visualize the electrostatic field lines to aid in positioning of the secondary electrode to direct the jets toward the grounded collector. The calculated potentials were made dimensionless by dividing the local potential by the potential difference between the rod and the grounded surface. The rod surfaces were set to a dimensionless
unit potential and the grounded surfaces set to zero dimensionless potential. Other boundaries in the solution space were modeled with the gradient of the potential normal to the surface set to zero.

The amount of fibers carried by the jets to the collector per unit time defines the production rate. Experimentally the production rates of the fibers were determined by weighing the amount of fibers collected on the grounded surface for specific time periods. The aluminum foil was weighed before and after electrospinning. The production rate was calculated with respect to the electrospinning time. All of the electrospun fibers were observed to collect on the aluminum foil collector; no fibers were observed to deposit on other surfaces in the experiments.

8.4 Summary and discussion

This part is going to describe the single rod electrospinning and multi rod array spinning method.

8.4.1 Single rod needless electrospinning experiment

Figure 8.4 shows example images of the single vertical rod, polymer jets, and fibers on the coaxial collector surfaces. SEM images of the fibers, the fiber diameter distributions, average fiber diameters, and production rates produced form the single vertical rod setup and the single syringe needle setup are summarized in Table 8.1.
The morphologies of the fibers were relatively smooth and without beads. The diameter distributions were similar between the vertical rod and the single-needle setups. The average fiber diameter produced by the vertical rod, $0.353 \pm 0.186 \mu m$, was larger than the average diameter by the single-needle, $0.295 \pm 0.144 \mu m$ but the standard deviations show significant overlap between the distributions.

The production rate by the vertical rod, $4.68 \pm 1.75 \text{ g/hr}$, was about 30 times greater than the production rate, $0.17 \pm 0.018 \text{ g/hr}$, by the single-needle. This shows that the multiple jets of the vertical rod method can significantly increase the rate of producing electrospun fibers.

Figure 8.4 (A) Photograph of single vertical rod with dried polymer jets extending from the rod to a coaxial grounded wire mesh collector. (B) Electrospinning jets launched from the surface of the vertical rod during electrospinning. (C) Photograph of electrospun fibers collected on a metal sheet from a vertical rod suspended from a PVC pipe cap.
Table 8.1 Comparison of single vertical rod and single-needle electrospinning performances. The +/- errors show one standard deviation of the calculated values.

<table>
<thead>
<tr>
<th>Process</th>
<th>Single Rod Needless Electrospinning</th>
<th>Single Needle Syringe Electrospinning</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM Image</td>
<td><img src="image1" alt="SEM Image" /></td>
<td><img src="image2" alt="SEM Image" /></td>
</tr>
<tr>
<td>Fiber Distribution</td>
<td><img src="image3" alt="Frequency Distribution" /></td>
<td><img src="image4" alt="Frequency Distribution" /></td>
</tr>
<tr>
<td>Average Diameter</td>
<td>353 ± 186 nm</td>
<td>295 ± 144 nm</td>
</tr>
<tr>
<td>Production Rate</td>
<td>4.68 ± 1.75 g/hr</td>
<td>0.17 ± 0.02 g/hr</td>
</tr>
</tbody>
</table>

Figure 8.5(A) shows a plot of the electric field current density and Figure 8.5(B) shows the contour plot of the dimensionless potential field for the single vertical rod within a coaxial cylindrical collector. The electric field for the rod and co-axial cylinder geometry is trivial but these plots are shown here to provide a basis for comparing with the field surrounding the rod arrays.

The colored arrows in Figure 8.5(A) indicate the direction of the current density vectors and the length of the arrows are proportional to the magnitude of the vectors. The black arrows (inserted by hand) indicate the prevailing directional
path of the vector arrows. As expected, the vectors symmetrically point from the center of the rod towards the grounded collector positioned axi-symmetric to the rod. The magnitudes decrease proportionally to the inverse radius squared and the lengths of the arrows diminish towards singular points as the distance from the rod increases. The concentric circles in Figure 8.5(B) indicate the uniformity of the potential field with coordinate angle and the decrease in the dimensionless potential from 1 to 0 with radial distance between the rod surface and the grounded collector.

Figure 8.5 (A) Electric field current density vector with circular collector. The black arrows were hand drawn indicating the prevailing vector field. (B) Contour plot for potential profile. The colors via the scale bar indicate the magnitude of the potential field.
8.4.2 Rod array electrospinning with secondary electrode

The analogous electrospinning setup of a single rod surrounded by the grounded collector applied to a linear array of rods could be designed with the collector designed as two parallel rectangular collectors connected with half cylinders at each end. This design, while possible, is not necessarily practical or convenient in some applications. Instead, a flat rectangular collector was located on one side of the array, parallel to the axes of the rods. A rectangular secondary electrode was positioned on the opposite side of the parallel rods to direct the fibers towards the grounded collector.

A top view of the design is shown in Figure 8.6. The design was modeled using FlexPDE, as before. Based on the vector and potential fields, a particular design was selected for testing experimentally. As shown in Figure 8.6, the design had the characteristic distance, D (6 cm in our experiments), between the rods. The secondary electrode was positioned at the same distance, D, from the plane of the rod axes. The ends of the secondary electrode were extended beyond the end rods by the distance D and wings were added to the secondary electrode that extended to the plane of the rod axes. The distance from the plane of the rod axes to the grounded collector was 3.33D (ie. 20 cm).

The width of the collector was the same in all of the rod array experiments with secondary electrode (4D) and the centerline of the collector was positioned symmetrically with the array of rods. The length of the secondary electrodes and the collectors were equal to the length of the rods (50 cm). Other configurations are possible and are left to future work for optimization.
Figure 8.6 Top view of setup for array of multiple rods with secondary electrode.

The current density vectors and the potential contour plots are shown in Figure 8.7 for 1, 2, 4, and 5 rod linear arrays as described in Figure 8.6. It is evident that the current density vectors were suppressed between the secondary electrodes and the vertical rods while the arrows were directed towards and converged at the surface of grounded collector.
Figure 8.7 FlexPDE™ 2D simulation of the electrostatic field around 1, 2, 4, and 5 rod arrays and secondary electrodes. The distance between rods, D, and the size
of the grounded collector, 4D, were the same between the simulations. (A) Current density vectors show the direction of potential field. The black arrows were hand drawn emphasizing the prevailing vector field. The secondary electrodes and collector were hand drawn to show the geometry. The inset image shows the FlexPDE™ grid. (top right inset : configuration plot for the position of rods, secondary electrode and collector). (B) Contour plot of potential profiles.

Figure 8.8 shows images of the two-rod setup before and after electrospinning (for the image in (B) the collector foil was turned slightly towards the camera for a better view of the surface). The collector foil between the two images clearly shows the white fiber mat on the collector after 15 minutes of electrospinning. The potential applied to the rods was 50kV and the potential applied to the secondary electrode was 30kV (60% of the potential applied to the rods). No fibers were observed on the secondary electrode.
Figure 8.8 Photographs of the two rod electrospinning setup showing the fibers on the collector. The collector and secondary electrode shown here were rotated for easier viewing, but during the experiment they were positioned consistent with Figure 8.6 (A) Before electrospinning. (B) After electrospinning. Fiber samples taken from points (1), (2), and (3) on the collector surface were analyzed for fiber size distributions.

To understand the fiber morphology and diameter along the rod axis (z-direction), the fiber sizes were measured. Figure 8.9 shows that the smallest fibers were observed in top position (1) of fiber mat [Figure 8.8(B)] with 229nm of average diameter. Furthermore, the fiber size distribution curve was shifted towards larger fiber sizes in the range of 200-600nm with size measurement of different position (middle (2) and bottom (3) of the fiber mat). The variations in size are consistent with evaporation of solvent from the drop causing the polymer concentration in the drop to increase with distance as the drop slides down the rod. In practical
applications this effect should be taken into account when selecting the rod length. In applications in which variation in fiber size distributions are desired this may be a simple and convenient method.

![Figure 8.9 Fiber size distribution for different position [top(1), middle(2), and bottom(3)] images of the fiber mat as shown in Figure 8.8(B).](image)

Table 8.2 summarizes the results of the experiments with 1, 2, 4, and 5 rods in the linear arrays with the secondary electrode. The mean fiber diameters for the different configurations were within one standard deviation of that of the single rod with no secondary electrode (Table 8.1) and the single needle electrospun fibers, indicating that the multiple rod setup did not significantly change the average fiber diameter. In other words, the fiber morphologies and sizes were unaffected by the method. However, the fiber size distribution of the diameter was varied in Table 8.2.
For the explanation of the difference among these fiber size distribution curves, One-way ANOVA analysis was carried out. The P-value was very close to 0 which is much less than $\alpha=0.05$, the test rejects the null hypothesis and concludes that the number of rods influences the distribution of fiber diameter significantly. Meanwhile, the size distributions determined from the SEM images shows that the fiber morphologies and average fiber diameters are not statistically affected by the quantity of rods used in experiments.

Table 8.2 Comparison of fiber produced by linear arrays of rods with the secondary electrode. The images are examples of fibers taken from the collector. The size distributions are calculated from the combined results of six samples collected from the three locations indicated in Figure 8.8(B).
The total production rate of fibers significantly decreased in comparison with the single rod in Table 8.1. This is due to the reduction in space available for the jets to launch and stretch into fibers. However, the production rate increased with additional rods, as shown in Figure 8.10.

The production rate of the single rod with co-axial cylindrical collector was significantly greater compared to other spinning setups, at a rate of about 4.5g/hour under applied voltage of 35kV. With the co-axial setup the fibers collected over the surface of the large co-axial cylindrical collector. Another way to compare the production rate is mass per hour per area of collector. The areas of the collectors were taken as the surface areas that visibly had fibers collected on the surface. Figure 8.10(B) shows the production rates per area. The linear array of 5 rods using flat collector (1200cm²) produced the highest concentration of polymer fibers per unit time of 0.001 g/hr per cm². The production rate per area of linear array of multiple rods using a flat collector increased directly with the number of rods. In future work experiments are needed to vary the distance between the rods and the size of the collector to optimize the performance.
Figure 8.10 Production rates of the different electrospinning setups. (A) Total production rate (sum of all of the rods in the arrays). (B) Total production rate per unit area of collector. The effective collector area of the single syringe setup was taken to be the projected area of the rotating drum (length x diameter). The areas of the array setups were the length x width of the collector, and the area of the coaxial setup was the circumference x length of the collector.

For quantitative assessments of correlation between the arrays of rods and their production rate, One-way ANOVA analysis was performed to evaluate the difference between the rod arrays and corresponding production rates with significance calculated. Since the P-value 0.047 is less than the selected $\alpha=0.05$, it statistically verifies that the number of rods significantly affected the production rate. Similarly, the difference of production rate in terms of single rod setup and one-rod with the secondary electrode was quantified by the same analysis, the P-value was 0.0022, much less than 0.05, which indicates production rate significantly changed with change of collector area. Moreover, this result implies
that the use of secondary electrode exerts a considerable impact on the electrospinning performance.

8.5 Conclusions

A needless vertical rod electrospinning method was successfully applied to fabricate polymer electrospun fibers. Multiple polymer jets were launched from the surface of the vertical rod electrode. The fiber morphologies and fiber sizes were unaffected by the method (syringe or rod) but the total production rate of fibers was significantly greater with the vertical rods.

The single vertical rod with co-axial cylindrical collector had the greatest total fiber production rate of about 4.5 g/h and the single needle had the least production rate of 0.17 g/h. The vertical rods in arrays with secondary electrodes to direct the fibers towards a smaller planar collector surface had total production rates greater than the single needle and the 5 rod production rate per area of collector surface of was higher than that of the single rod with co-axial cylindrical collector.

8.6 Acknowledgement of prior publication of the work described

The contents of this chapter were published in reference [114]. The journal allows the paper to be republished as part of a thesis according to their website [220].
9.1 Conclusion

1. Submicron sized $\text{Al}_2\text{O}_3$ fibers were formed by calcination of electrospun aluminum acetate/PVP composite fibers. At 650°C the fibers were amorphous. As calcination temperature increased the alumina fibers compositions transitioned from amorphous to increasing crystallinity of gamma phase alumina. At calcination temperature of 1000°C some of the gamma crystallites transformed to alpha phase. In concurrence with changes in crystal phases the fiber morphologies and pore structures changed. The average fiber diameter decreased from 330 to 140nm. The specific surface area increased from 9 m$^2$/g at 650°C to 151 m$^2$/g at 850°C followed by a decrease to 33 m$^2$/g as the temperature further increased to 1000°C.

2. Sub-micron sized alumina fibers were fabricated by electrospinning and calcination of a polymer template fiber. In the calcination step, different controlled temperature heating cycles were conducted to obtain fibers of different crystalline structures. Their biodurabilities were tested at pH 7.4 with lung airway epithelial lining fluid or serum ultrafiltrate (SUF) and at pH 4.5 with macrophage phagolysosomal simulant fluid (PSF). Through the variation in the soak
temperature from 650°C to 950°C (experiments S650-S950), the heating protocol affected the morphological characteristics, crystal structure, surface area, and density of the alumina fibers while their dissolution half-times were not significantly affected in SUF or PSF. Fiber samples formed at different heating ramp rates (experiments R93-R600) showed significant variation in the dissolution rates with the highest ramp rate corresponding to the highest dissolution rate. Thus, by increasing the calcination temperature ramp rate the alumina fibers may be produced that have reduced biodurability and lower inflammogenic potential. The fibers with the highest dissolution rated had the least aluminium content. The solubility half-times of the alumina fibers were shortest for fibers calcined at the fastest temperature ramp rate (though soak temperature did not have an effect). The ramp rates also affected the aluminium content of the fibers suggesting that the content may affect the structural strength of the fibers and control the dissolution.

3. The Pd/Al₂O₃ fibers were prepared over a range of calcination temperatures and tested for comparison of their performances. The Pd particles had a sizes ranging from 5 – 20 nm and appeared randomly distributed within and near the surfaces of the alumina fibers. As calcination temperature increased the alumina crystal structure changed from amorphous at 650°C to alpha crystal structure at 1150°C. With the increase of calcination temperature the average fiber diameters and specific surface areas decreased. The fiber media had good conversion of NO and CO gases. Higher calcination temperatures led to higher reaction temperatures from 250 to about 450°C for total conversion, indicating the
effective reactivity of the fiber-supported catalysts decreased with increase in calcination temperature. The fibers formed at the 650°C calcination temperature had the highest reaction activity.

4. Pd-Au nano-sized alloy catalysts supported on titania submicron-sized fibers have been developed by electrospinning, calcination of the polymer template fibers, and hydrazine reduction. The morphologies, crystal structure, and textural properties (surface area, pore size, and volume) of Pd-Au/TiO2 fibers materials were evaluated with electron microscopy (SEM, TEM, and HRTEM), X-ray Diffraction (XRD), and Brunauer, Emmett and Teller (BET) nitrogen adsorption. For the alloy effect induced by the Pd-Au formation, the ensemble (geometric) effect and ligand effect (charge transfer) in Pd-Au nanoparticles were investigated with X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) to understand the formation of alloyed Pd-Au particles of different metal composition with consequent modification of their electronic and geometric properties. For XPS characterization, binding energy shifts were detected due to chemical bonding and reduction with hydrazine monohydrate.

The fiber media with Pd-Au nanoparticles had greater reactivity in conversion of NO and CO gases than Pd monometallic catalyst alone, attributed to a lower activation energy of the reaction on the Pd-Au catalyst particles. For CO oxidation tests, the performance was optimal for a catalyst of composition Pd\textsubscript{2}Au\textsubscript{1} molar ratio that was active at 125°C, which had higher dispersion of active components and better catalytic performance compared to monometallic particle Au/TiO\textsubscript{2} and
Pd/TiO$_2$ fiber media. Moreover, the improved reaction activity of Pd$_2$Au$_1$/TiO$_2$ fiber medium was attributed to a decreased in the activation energy.

5. Most electrospinning applications employ charged needles or nozzles but have low production rates. For higher production rates several needleless systems have been developed. In chapter 8, we reported on a simple unique needleless method that employs charged vertically oriented threaded rods for holding multiple drops to launch many simultaneous jets. Experiments were conducted with a single rod or multiple rods arranged in a linear array. The direction of the launched jets was controlled using a secondary electrode to direct the jets towards the grounded collector. Results show a single rod of about 50cm in length can produce PVP fibers at a rate of 4.5 g/hr and 200-400 nm size range.
9.2 Future work

Catalytic performance study

1. The results reported show a synergistic effect between Au and Pd on the titania support fibers. In some practical applications oxygen, water, or CO$_2$ may be present in the inlet gas stream.

2. The effects of compounds on the performance should be considered in future work. Stability of the catalyst is important for practical applications and should be explored.

3. Future work should also compare performances of the imbedded catalyst particles via the electrospinning to the performance of supported catalysts formed using conventional methods such as wet coating.

4. Au atoms in the vicinity of Pd atoms may prevent Pd aggregation and lead to higher stability of the Pd ensemble in Pd$_4$Au$_1$ catalysts as reported in literature [165]. The reverse may also be possible, that the Pd atoms may prevent aggregation of Au atoms.

5. The effect of aggregation should be explored in future work, particularly because the submicron fiber structure restricts the potential particle movement to aggregate to one-dimensional movement along the fiber axis in contrast to two-dimensional movements that are possible on larger structures. The aggregation mechanism is one of several that may affect the useful lifetime of the catalyst structure.
6. Density functional theory (DFT) calculation should be performed in future work to investigate CO oxidation Pd-Au bimetallic (111) surfaces.

7. Durability tests should be conducted and compared with other supported catalysts and structures as part of future work.

Bio-durability study

1. Further work should be conducted to determine how the temperature ramp rate affects the crystal structure of the alumina and how fiber diameter affects the temperature variation within the fiber during heating.

2. The different types of engineered nanomaterials should be considered in artificial lung fluid models.
REFERENCES


[109] A. Stefaniak, Particle and Fibre Toxicology, 7 (2010) 38.


TIO2 FIBER CHARACTERIZATION STUDY

Figure A.1 shows SEM (A) and TEM (B) images of Titanium isopropoxide/PVP composite fibers and those fibers calcined at different controlled heating cycles. It can be observed from the SEM images (Figure A.1[A]) that the fibers were continuous without any beads and the fibers were randomly oriented as produced from the electrospinning process [221]. The TEM images(Figure A.1[B]) indicate a surface change of fiber samples during the heating process. The PVP fiber sample (Non-calcined fibers) showed smooth and homogeneous surfaces. Whereas, the surface of the fibers (calcined from 650 to 950°C) became rough due to the development of grain boundaries. In Figure A.1(B) the S750 and S850 TiO$_2$ fibers showed a wrinkled structure on the surface and had ultrafine grain size in the range of 20-80nm. By calcination to 950°C the image of the S950 sample fibers shows the surface to be composed of 150nm of grain size.

This result shows that grain size of fiber composites were smallest for fibers calcined at 650°C and gradually increased in size when calcined at 950°C due to coalescence of the grains. The average grain sizes of fibers calcined at 650, 750, 850, 950 °C were 24, 52, 85, and 178 nm respectively. Based on the experimental result, the grain growth of electrospun fibers with different calcinations process can
be proposed and modified in fiber morphology. For the different ramp rate of TiO2 fibers (R93, R204...R600), the morphologies appears to not have significantly changed among these fibers.

Figure A.1 SEM (A) and TEM (B) images of variation in soak temperatures (samples labeled PVP01, S650 to S950) and heating ramp rates (samples labeled R93, R204, R315, and R600).
Figure A.2 shows the fiber diameter distribution and average diameter of TiO$_2$ fibers calcined at different heating cycles. Figure A.2 corresponds to the SEM image of Figure A.1(A). The fiber diameter distribution trend was to become more narrow and the average fiber diameter decreased as the calcination temperature increased Figure A.2(A). This trend was consistent with observations reported in literature[222]. For different ramp rate of fiber diameter in Figure A.2(B), there was no significant change.

Figure A.2 Fiber diameter distributions and average diameters (inset). (A) Variation in soak temperatures (samples labeled PVP01, S650 to S950). (B) Variation in heating ramp rates (samples labeled R93, R204, R315, and R600).

Figure A.3 shows XRD diffraction patterns of TiO$_2$ fibers calcined at different temperature cycles. The Crystal structure data of TiO$_2$ fiber was also shown in Table A.1. First, PVP01 fibers were amorphous phase on the sample before calcination. At 650°C, rutile-anatase mixture phase TiO$_2$ fibers(S650) were formed. And then, the XRD patterns of S750-S950 samples were transformed into
complete rutile phase as the heat-treatment temperature increased to 950°C as shown in Table A.1. Therefore, the crystalline size and peak intensity can be tuned by changing the soak temperature [223, 224]. The average crystalline sizes of S650, S750, S850, and S950 were 13, 15, 24, and 18nm, calculated from the (110) diffraction peak of rutile.

Figure A.3 XRD Patterns of TiO$_2$ fibers calcined at different heating cycles.
For X-ray patterns of different ramp rate samples at soak temperature 650°C (i.e. the fibers calcined at the various ramp rates R93, R204...R600), two mixed crystal phases appeared. A slow ramp rate (R93) gave a higher anatase content relative to rutile. With the increase of ramp rate from 93 to 600°C/hr (R93-R600), the anatase phase content decreased as shown in Table A.1. Thus, the XRD and TEM [Figure A.1B(R93-R600)] results indicate that the crystal transformation from anatase to rutile phase could be initiated from ultrafine grains between the anatase particles in the TiO₂ fiber [225, 226]. In comparison with inset image of Figure A.1B (R93-R315), the grain growth in size of grains of TiO₂ fibers was confirmed in inset image of Figure A.1B (R600, phase content 97:3 of rutile:anatase). TEM and XRD analyses show that the increase ramp rate from 93 - 600°C/hr can reduce the anatase phase content, increase the rutile content, and increase the grain size.

Table A.1 Crystal phase, phase content, and crystallite size of TiO₂ fibers.

<table>
<thead>
<tr>
<th>Material</th>
<th>Rampᵃ (°C/hr)</th>
<th>Tcalcine (°C)</th>
<th>Crystal Phases</th>
<th>Mass fractionᵇ (Rutile:Anatase)</th>
<th>Averageᶜ Crystallite Size(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP01</td>
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<td>N/A</td>
<td>Amorphous</td>
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<td>N/A</td>
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<td>Rutile+Anatase</td>
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<tr>
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<td>Rutile</td>
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<td>18</td>
</tr>
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<td>Rutile+Anatase</td>
<td>79:21</td>
<td>21</td>
</tr>
<tr>
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<td>650</td>
<td>Rutile+Anatase</td>
<td>80:20</td>
<td>18</td>
</tr>
<tr>
<td>R600</td>
<td>600</td>
<td>650</td>
<td>Rutile+Anatase</td>
<td>97:3</td>
<td>13</td>
</tr>
</tbody>
</table>
Figure A.4 shows the specific surface areas and density for all of the samples. The calculated BET surface area and density were in the range of 4 - 10 m$^2$/g and 1.5 - 4.5 g/cm$^3$ for all calcined fibers. Samples exhibit a relatively low surface area and density.

Figure A.4 Specific surface area (Top) and density (Bottom) of TiO$_2$ fibers calcined at different heating profile.
## APPENDIX B

### COMPOSITIONS OF ARTIFICIAL LUNG FLUIDS

#### Table B.1 Serum ultrafiltrate (SUF).

<table>
<thead>
<tr>
<th>Constituent</th>
<th>g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride (NaCl)</td>
<td>6.7790</td>
</tr>
<tr>
<td>Ammonium chloride (NH₄Cl)</td>
<td>5.3490</td>
</tr>
<tr>
<td>Sodium bicarbonate (NaHCO₃)</td>
<td>2.2683</td>
</tr>
<tr>
<td>Sodium dihydrogen phosphate hydrate (NaH₂PO₄·H₂O)</td>
<td>0.1656</td>
</tr>
<tr>
<td>Sodium citrate dihydrate (Na₃citrate·2H₂O)</td>
<td>0.0588</td>
</tr>
<tr>
<td>Glycine (C₂H₅NO₂)</td>
<td>0.3754</td>
</tr>
<tr>
<td>L-Cysteine hydrochloride</td>
<td>0.1756</td>
</tr>
<tr>
<td>DTPA [(HOOCH₂)₂NCH₂CH₂NCH₂COOH]</td>
<td>0.0787</td>
</tr>
<tr>
<td>Conc. Sulfuric Acid (H₂SO₄)</td>
<td>0.03 mL/L</td>
</tr>
<tr>
<td>Calcium chloride dihydrate (CaCl₂·2H₂O)</td>
<td>0.0294</td>
</tr>
</tbody>
</table>

#### Table B.2 Alveolar macrophage phagolysosomal fluid (PSF).

<table>
<thead>
<tr>
<th>Constituent</th>
<th>g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium phosphate dibasic anhydrous (Na₂HPO₄)</td>
<td>0.1420</td>
</tr>
<tr>
<td>Sodium chloride (NaCl)</td>
<td>6.6500</td>
</tr>
<tr>
<td>Sodium sulfate anhydrous (Na₂SO₄)</td>
<td>0.0710</td>
</tr>
<tr>
<td>Calcium chloride dihydrate (CaCl₂·2H₂O)</td>
<td>0.0290</td>
</tr>
<tr>
<td>Glycine (C₂H₅NO₂)</td>
<td>0.4500</td>
</tr>
<tr>
<td>Potassium hydrogen phthalate (1-(HO₂C)-2-(CO₂K)-C₆H₄)</td>
<td>4.0846</td>
</tr>
</tbody>
</table>