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# Abstract

Pd-Au nano-sized alloy catalysts supported on Titania (TiO<sub>2</sub>) submicron-sized fibers were fabricated by calcination of electrospun polymer template fibers and hydrazine reduction. The morphologies, crystal structure, and textural properties (surface area, pore size, and volume) of Pd-Au/TiO<sub>2</sub> 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. The catalytic activities of the materials were tested in carbon monoxide oxidation reaction using a plug-flow reactor. The results showed that the performance was optimal for a catalyst of composition Pd<sub>2</sub>Au<sub>1</sub> 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<sub>2</sub> fiber media. Moreover, the improved reaction activity of Pd<sub>2</sub>Au<sub>1</sub>/TiO<sub>2</sub> fiber media was attributed to decrease in activation energy.

## **Keywords**

Nanofibers, Catalysis, Electrospinning, Conversion, Oxidation

# 1. Introduction

Metallic nanoparticles are gaining extreme interest due to their wide range of applications in molecular electronics, photo-electronic devices, and catalysis [1-4]. 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 [5]. Pd–Au bimetallic heterogeneous catalysts is one of the most important bimetallic catalysts. Pd–Au catalysts are used in the industrial production of vinyl acetate (VA) [6-7]. It has also been successfully used to catalyze many reactions like direct  $H_2O_2$  synthesis from  $H_2$  and  $O_2$  [8-9], hydrodechlorination of Cl-containing pollutants in underground water [10], hydrodesulfurization of S-containing organics [11], hydrogenation of phenol [12], and coupling of acetylene to benzene [13].

Alloying or combining two metals (eg. Pd-Au) can lead to materials with special catalytic properties due to three types of alloy effects: (1) different elementary reaction steps (bi-function effect), (2) the electron transfer among the two metals enhanced reactivity (ligand effect), and (3) the specific group of surface atoms developed by geometric growth (ensemble effect) [5], [14]. Goodman et al. reported these synergetic effects of Pd-Au alloy formation [15-17]. Furthermore, it is recognized and reported that there is a challenge to achieve high dispersion of either pure palladium or pure gold nanoparticles because these nanoparticles are easily reduced to form large metal particles due to their physical and chemical properties' effects during the activation processes (calcination or hydrogenation) [18]. The agglomeration of the nanoparticles into large metal particles results in poor metal dispersion, lower active surface area, and hence lowers catalytic activity.

Xu Yang and coworkers showed that the addition of palladium-gold to meso-porous hollow silica spheres (MHSS) improved 6 times the catalytic activity of phenol hydrogenation conversion reactions in comparison with Pd/MHSS [12, 18]. They attributed the high Pd-Au catalytic performance to the high dispersion of the active Pd component which is a result of the addition of Au and the interactions between the gold and palladium [12]. Samanta et al. also reported that particle size of Pd-Au nanoparticle appeared to correlate with the amount of Au in the alloy phase [19]. Metal dispersion is defined as the ratio between surface and total metal atoms, and generally metal dispersion should be as large as possible for best catalytic performance [20].

Catalytic activity of Pd-Au is dependent on the preparation method, the support type and the method of reducing the size of gold particles [21-22]. The deposition-precipitation (DP) method is a preferred method for making small gold particles [23]. For Au atoms of Pd-Au system, oxygen activation is expected to occur directly on the small size of gold particles [24].

Oxide vacancies formed near to the gold-support interface offer a site for oxygen adsorption [25]. CO oxidation fundamentally proceeds through the Langmuir-Hinshelwood mechanism and co-absorption of both CO and active oxygen is the most principal step [26]. Goodman group tested Pd-Au catalyst CO oxidation as a Langmuir-Hinshelwood type of reaction [5, 7, 15-17]. It is demonstrated that a sufficient amount of Pd segregates to the surface and generates contiguous Pd sites, which are capable of dissociating  $O_2$  to allow the CO<sub>2</sub> formation reaction [5, 15]. Moreover, the addition of Au can weaken the CO binding energy due to the charge transfer from Pd to Au [5, 19]. Thus, Pd-Au alloys can perform the CO oxidation more efficiently than pure Au and pure Pd catalyst at low temperature.

Typical preparation methods of heterogeneous catalysts 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 [27-29]. Electrospinning is a very useful technique to immobilize metal nanoparticles on polymeric or ceramic nanofibers. Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/TiO<sub>2</sub> and many other catalysts have been prepared using electrospinning [28-33]. In this work, different catalysts (Pd/TiO<sub>2</sub>, Au/TiO<sub>2</sub>, and Pd-Au/TiO<sub>2</sub>) were

prepared by electrospinning technique to compare their performances in CO oxidation. Further investigations were carried out to study the influence of the presence and content of the second metal (Pd or Au) on the Pd-Au alloy nanoparticle size and dispersion.

# 2. Experiments

#### 2.1. 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 & Chemical Company, Fisher Scientific, and Pressure Chemical, respectively. All chemicals were used as received without any further purification.

#### 2.2. Synthesis of PdCl<sub>2</sub> - HAuCl<sub>4</sub> / TiO<sub>2</sub>+PVP Electrospinning Solutions

There are four major steps to prepare the catalytic titanium fiber electrospinning solution. These steps are (1) preparation of a polymeric solution, (2) preparation of a ceramic precursor solution, (3) mixing of the polymeric and ceramic precursor solutions to form a polymeric – ceramic electrospinning solution and (4) addition of a catalytic metal precursor to the mixture that was prepared in step (3) to form the final metallic - polymeric – ceramic electrospinning solution.

First, 16 wt.% of PVP solution was prepared by dissolving PVP in a mixture of 10 mL ethanol, 10 mL DMF, and 10 mL acetone in a volume ratio of 1:1:1 respectively for 12hours to obtain a homogenous polymeric solution. Second, the ceramic precursor solution was prepared by mixing 6 mL titanium isopropoxide, 12 mL acetic acid, and 12 mL ethanol at a volume ratio of 1:2:2 respectively and stirred using a magnetic stirrer for 4 hours at room temperature. The polymeric and the ceramic precursor solutions were mixed together to make the electrospinning mixture and stirred for at least 1 hour prior to electrospinning.

Finally, 71.2 mg (0.40mmol) of palladium chloride (PdCl<sub>2</sub>) and 68.3 mg (0.20mmol) of gold chloride hydrate (HAuCl<sub>4</sub>) were added to the prepared electrospinning mixture and stirred overnight at 40°C using a magnetic stirrer. Pd<sub>1</sub>Au<sub>1</sub>, Pd<sub>1</sub>Au<sub>2</sub>, Pd, and Au, nanoparticles doped TiO<sub>2</sub> sub micron sized fibers were synthesized and electrospun with different amounts of PdCl<sub>2</sub> and HAuCl<sub>4</sub>, respectively.

#### 2.3. Preparation of PdCl<sub>2</sub> - HAuCl<sub>4</sub> / TiO<sub>2</sub>+PVP Fibers

Two plastic syringes (BD 5 mL syringe, Fisher Scientific) were filled with the electrospun solutions, and then installed into a syringe pump. The syringe pump, (SP101I, WPI), was adjusted to deliver a flow rate of 3  $\mu$ /min to the tips of two 21 gauge steel needles. A 25 kV DC electric potential was applied using a power supply (Gama High Voltage). When the

electric forces overcome the surface tension of the droplets, polymer jets were launched from the drops and directed towards a grounded rotating collector. When the polymeric solution travels towards the collector, the polymer jets elongate to submicron diameters and the solvents evaporate to form solid fibers on the grounded collector [34-37].

The collected electrospun fibers form a non-woven fiber mats. The mats were calcined at 550°C to remove the PVP polymers and convert the ceramic precursor fibers into  $TiO_2$  form. The PdCl<sub>2</sub> and HAuCl<sub>4</sub> were reduced to their metallic forms by reaction with hydrazine monohydrate [38-39]. After reduction, the fibers were washed using ethanol, and vacuum-dried at 80°C for 24 hours.

#### 2.4. Preparation of Catalytic Fiber Media

A vacuum molding process was used in this work to make cylindrical catalytic fiber media. The process was executed in three steps: a) preparation of a fiber slurry b) forming a wet fiber cake by vacuum molding, and c) drying the wet cake in a furnace.



**Figure 1.** Overall preparation procedures of 2.3 cm fibrous fiber media based on catalytic nanoparticles (Au, Pd, or Pd-Au) doped TiO<sub>2</sub> submicron sized fiber. Step (A): electrospinning solutions, Step (B): electrospinning, calcination, and reduction of only Au, Pd, or Pd-Au doped TiO<sub>2</sub> fibers, and Step (C): Final catalytic media out of catalytic submicron sized titania fibers and Alumina microfibers [(1) Au/TiO<sub>2</sub>, (2) Pd<sub>1</sub>Au<sub>2</sub>/TiO<sub>2</sub>, (3) Pd<sub>1</sub>Au<sub>1</sub>/TiO<sub>2</sub>, (4) Pd<sub>2</sub>Au<sub>1</sub>/TiO<sub>2</sub>, and (5) Pd/TiO<sub>2</sub>].

Figure 1 shows pictures for the solution mixtures and materials at each step in the preparation of the fiber media containing the catalytic nanoparticle doped  $TiO_2$  submicron fibers. First, a liquid slurry was prepared by mixing 0.5 gm of chopped alumina microfibers (Saffil HA bulk fibers, Thermal Ceramics), 0.05 gm of Pd-Au doped titania submicron-sized fibers (synthesized in this work as described above), 0.02 gm

of corn starch, 0.5 mL of binder (Megasol S50, Wesbond Corporation), 20 drops of dilute  $H_2SO_4$  acid and 4 L of water. Here, the alumina microfibers were used to support the TiO<sub>2</sub> nanofibers. The acid was added to the slurry to adjust the slurry to a pH of 6.0 to aid in dispersing the fibers and the starch was added to enhance the binding between the fibers. The liquid was drawn through the mold by vacuum pressure with the aid of a vacuum pump. The fibers were retained on the steel mesh covered by the filter paper to form the fibrous wet cake. The mold was cylindrical with a diameter of 2.3 cm to form a wet cake 2.3 cm in diameter and about 1 cm in depth. Finally, the wet cake was heated to 500°C to dry the cake and bind the fibers together.

#### 2.5. CO Oxidation

The catalytic fiber media was placed in a steel reactor with a 2.3 cm diameter hole to hold the catalytic sample. The reactor was wrapped with a heating tape (Omega FGS051-060) connected to a temperature controller (Micromega CN77000). The reaction gases consists of 98% He, 1% NO and 1% CO 1 mol/ mo. The volumetric flow-rate of upstream gases was set at 100 sccm. Three independent experiments were conducted with same gas concentrations and upstream flowrates to ensure reproducibility of test data. An elaborated flow diagram of the laboratory set up was reported in [4]. Upstream and downstream gas concentrations were measured using gas chromatography (TCD GC, SRI 8610C). Peak Simple software (Version 3.29) was used to display the peaks calculate the concentrations of the chemical components of the reaction gases.

The CO conversions were calculated using the following:

$$X_{a}(\%) = \frac{F_{a}^{in} - F_{a}^{out}}{F_{a}^{in}} \times 100$$
(1)

where  $F_a^{in}$  and  $F_a^{out}$  are the inlet and outlet molar flow of gas "a", respectively.

The disappearance rate  $(-r_a)$  of CO per mass of catalyst, was calculated using the following [40]:

$$-r_{a}^{'} = \frac{F_{a,0} \cdot X_{a}}{\Delta W_{cat}} = \frac{[a]_{0} \cdot v_{0} \cdot X_{a}}{\Delta W_{cat}} = \frac{v_{0}}{\Delta W_{cat}} \cdot \frac{P_{T}}{RT} \cdot X_{a}$$
(2)

Where  $F_{a,0}$  is the entrance molar flow rate of gas a,  $X_a$  is the conversion of gas a,  $\Delta W_{cat}$  is the amount of catalyst,  $[a]_0$  is the entrance concentration of gas, and  $V_0$  is the entrance volumetric flow rate. The disappearance rate  $(-r_a^{"})$  of CO was calculated using the equation  $(-r_a^{"}) = -r_a / S_{metal}$ , where  $S_{metal}$  is the specific surface area of the Pd and Pd-Au nanoparticle catalysts. The turnover frequency (TOF) for CO was calculated as defined by [40]:

Where  $N_A$  is Avogadro's number and  $\dot{S}$  is the surface atom density of Pd-Au nanoparticles were calculated using molar ratio and lattice constant [40].

#### 2.6. Characterization

Scanning electron microscope (FEI Quanta 200 at 30 kV, HITACHI TM3000 at 15 kV) images were analyzed to study the fiber morphology and FibraQuant software (Version 1.3, nanoScaffold Technologies LLC, Chapel Hill, NC, USA) was used to determine the diameter distributions of the electrospun fibers and metallic nanoparticles. Transmission Electron Microscopes (TEM, JEM 1200XII and HRTEM, FEI Tecnai G2 F20) were used to study catalytic particle size and morphology of Pd-Au doped TiO<sub>2</sub> nanofibers. Fiber samples were diluted in ethanol and deposited on a carbon lacey film coated copper grids and dried at 70°C for 30mins. Carbon film acts as a substrate to hold more fibers on individual grids and most of the fibers were self-supported by the tiny holes. Fast Fourier Transform (FFT) tool was applied to the HRTEM images to study crystallinity of the fibers. Energy dispersive X-ray analysis, EDX (Bruker Quantax70) was used for elemental quantification analysis. It was designed to run on the SEM HITACHI TM3000 simultaneously.

X-ray diffractometer (Bruker AXS Dimension D8 X-ray) was used to determine the crystal phase, the crystallinity, and the crystal size of the samples. A Cu anode (K $\alpha_1$  = 0.154056 nm) was used. The voltage was set to 40 kV whereas the current was set to 40 mA. Scans were collected with the step size of 0.1 deg and scan speed of 0.5 deg/min.

The Brunauer, Emmett and Teller (BET) surface area of materials was measured using nitrogen gas adsorption. Each sample was dried in a clean dry tube at 100°C for 4 hours in a degas station (Micromeritics VacPrep 061) to remove the moisture from the samples. The combined mass of the sample tube and stopper was determined to 0.1 mg precision using a calibrated microbalance (AX205, Mettler Toledo). Surface area was measured using Surface Area and Porosity Analysis Instrument (Micromeritics Tristar II). A value of 0.162 nm<sup>2</sup> was used for the molecular cross-sectional area of N<sub>2</sub> at 77 K.

High resolution X-ray photoelectron spectroscopy (PHI Versa Probe II Scanning XPS Microprobe) was used for investigating the chemical composition and chemical bonding through measurement of chemical shift. The analyzer pass energy was 23.5 eV for the high-resolution  $Pd_{3d}$  and  $Au_{4f}$  scans. The XPS spectra were recorded at a takeoff angle of 45°. Automated charge neutralization was used during the analysis of the samples to provide accurate data. Samples were analyzed under ultrahigh vacuum, at a pressure of 1X10 -6 Pa. Each spectrum was collected using a monochromatic (Al Ka) X-ray beam (E = 1486 eV) over a 200 mm diameter probe area. Curve fitting of the peaks was performed by the PHI MultiPak software, applied the Shirley background correction method.

Fourier transform infrared spectroscopy (FTIR) was carried out by a Thermo Scientific Nicolet 6700 spectrometer for studying CO adsorption with Au, Pd, and Pd-Au alloy nanoparticles was obtained by recording the absorbance as a function of wavelength. 1cm X 1cm test samples were sandwiched in between KBr pallets and background was corrected for normalization. Adsorption of CO was measured in 655 Pa equilibrium pressure, followed by evacuation at 293K. To normalize the IR measurements the single beam signal (I) from overall sample is divided by the KBr background signal (Io). The result is a %-transmittance spectrum (T = I/Io) was obtained at room temperature and a total of 64 scans were averaged in to one single beam spectra.

#### **3. Results and Discussion**

Figure 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 fibers diameters was measured from at least 10 images. The SEM images of Pd-Au/ $TiO_2$  fibers were obtained for media with different nanoparticle compositions as indicated by the subscripts on the metal symbols showing the ratio number of atoms of each metal in the original electrospinning mixture. In Figure 2, the morphologies of the electrospun fibers were observed in SEM images and show the fibers do not have beads. The histograms 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 about 110nm. See Table 1 for more details.

The TEM images in Figure 2 (Right column) show the metal nanoparticles were well dispersed within and near the surface of the TiO<sub>2</sub> fibers, which had a nanoparticle diameter of 19.8 nm for Au/TiO<sub>2</sub>, 14.2nm for Pd<sub>1</sub>Au<sub>2</sub>/TiO<sub>2</sub>, 9.3 nm for Pd<sub>1</sub>Au<sub>1</sub>/TiO<sub>2</sub>, 7.2nm for Pd<sub>2</sub>Au<sub>1</sub>/TiO<sub>2</sub>, and 8.5 nm for Pd/TiO<sub>2</sub>, respectively, detailed measurements are reported in Table 1. This shows that the particle size may be effectively controlled by the amount of Au added to the electrospinning mixture. Once the ratio of Pd<sub>1</sub>Au<sub>2</sub> changed to Pd<sub>2</sub>Au<sub>1</sub>, the metal particles size became smaller, which is in good agreement with the reported literature [18]. Furthermore, the Pd-Au nanoparticles were firmly embedded in the TiO<sub>2</sub> nanofibers by electrospinning, calcination, and reduction processes. The monometallic particles of Au and Pd, gave different peak positions in the XRD measurements than the alloy structure Pd-Au particles, as discussed in the next section.

To investigate the elemental composition of samples with different metallic nanoparticles, SEM-EDX mapping was performed and sample images are shown in Figure 3. These images show the Pd and Au nanoparticles were well distributed on the surface of the TiO<sub>2</sub> fibers. The measured Pd-Au particle compositions (atomic ratios) are approximately similar with the ratios of the metal precursors, indicating that reductions of both precursors were successfully carried out after calcination process. The mass percentage of total metal loading was in range of 4.8-5.3%.



**Figure 2.** SEM micrographs (left column) with  $2\mu$ m scale bar, associated fibers size distributions (center column) and TEM images (right column) with 100 nm scale bar. Fiber size distributions (right column) calculated from multiple images. Fiber materials marked by labels (metals/fiber structure): (A) Au/TiO<sub>2</sub>, (B)  $Pd_1Au_2/TiO_2$ , (C)  $Pd_1Au_1/TiO_2$ , (D)  $Pd_2Au_1/TiO_2$ , and (E)  $Pd/TiO_2$ . Subscripts on the metal symbols indicate the atomic ratio of metal atoms in a two metal blend (i.e.,  $Pd_2Au_1$  means 2 atoms Pd to 1 atom of Au in the preparation mixture).





Figure 3. SEM-EDX mapping of Pd<sub>2</sub>Au<sub>1</sub>/TiO<sub>2</sub> fibers.

| Table 1. I | Fiber size, | particle size, | composition | and metal | l loading |
|------------|-------------|----------------|-------------|-----------|-----------|
|------------|-------------|----------------|-------------|-----------|-----------|

| Material  | Fiber size<br>(nm) | Particle<br>size (nm) | Particle<br>composition | Metal<br>loading (wt %) |
|---|--------------------|-----------------------|-------------------------|-------------------------|
| Au/TiO <sub>2</sub>                               | 119±53             | 19.8±1.9              | Au                      | 5.3                     |
| Pd <sub>1</sub> Au <sub>2</sub> /TiO <sub>2</sub> | 124±57             | 14.2±1.7              | Pd35Au65                | 4.9                     |
| Pd <sub>1</sub> Au <sub>1</sub> /TiO <sub>2</sub> | 107±51             | 9.3±1.1               | Pd52Au48                | 4.7                     |
| Pd <sub>2</sub> Au <sub>1</sub> /TiO <sub>2</sub> | 99±49              | 7.2±0.8               | Pd68Au32                | 5.0                     |
| Pd/TiO <sub>2</sub>                               | 105±55             | 8.5±0.6               | Pd                      | 4.8                     |

To further study the comparison before and after the reduction process for Pd-Au nanoparticles on the  $TiO_2$  fibers, HRTEM images of the two samples are shown in Figure 4. Crystalline PdO peaks could not be identified in the HRTEM image of Figure 4(A). However, a very thin amorphous layer was visible at the surface of the particles, suggesting an oxide layer may have formed on the particles after the calcination process in air.



**Figure 4.** HRTEM images of electrospun Pd<sub>2</sub>Au<sub>1</sub>/TiO<sub>2</sub> fiber (A) after calcination in air at 550°C for 4 hours (B) after consequent reduction using hydrazine, washed and vacuum dried at 80°C. The inset in (B) shows the FFT pattern corresponding to the particle in the HRTEM images.

In Figure 4(B), the HRTEM image depicts the  $Pd_2Au_1/TiO_2$ fiber after the reduction, washing, drying, and the samples were analyzed under 5-mbar high vacuum. 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. This was verified by XPS data in the next section. In addition, the crystallinity of the Pd-Au nanoparticles in Figure 4(B) was clearly visible with 0.291 nm 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.



Figure 5. XPS peaks of Pd 3d (A) and Au 4f (B) after and before reduction. Reprint copyrights obtained from our previous work [4].

To verify the above explanation, X-ray photoelectron spectroscopy (XPS) was used for analysis of chemical bonding before and after reduction with hydrazine monohydrate. The high-resolution XPS spectra corresponding to Pd3d and Au4f binding energy regions (330-350 eV and 80-90 eV, respectively) are shown in Figure 5. The Pd 3d spectra before the reduction process reveal that multiple oxidation states of palladium exist in 3 different chemical environments. Before reduction, both Pd3d doublet peaks were fitted with 3 components corresponding to metallic Pd, PdO and PdO<sub>2</sub>. The energies for the  $3d_{5/2}$  peak were at 334.7, 335.9, and 337.8 eV, respectively, as shown in Figure 5(A). It can be observed that after calcination of electrospun PdCl<sub>2</sub> + HAuCl<sub>4</sub> / TiO<sub>2</sub>, the PdO and PdO<sub>2</sub> spectral peaks were dominating, while a smaller amount of metallic Pd was also present. These values are in good agreement with the reported binding energy [5], [41-43]. After reduction using hydrazine, the PdO and PdO<sub>2</sub> presence was not detected and only

palladium metallic peaks were observed at 334.5 and 340 eV. In Figure 5(B), the XPS peaks in the case of gold were attributed to Au  $4f_{7/2}$  at 83.0eV and  $4f_{5/2}$  at 86.8 eV. As a result of the reduction process, Au4f peaks shifted towards lower binding energies by 0.26 and 0.25 eV, respectively. In comparison with pure Au XPS peaks (84.0 and 88.0 eV)[44-45], the shift in binding energy to the lower energy side is even more pronounced. This negative shift of about 1.00 eV of our nanoparticle Au4f peaks from monometallic Au4f peaks might be explained by the addition of Pd to the catalyst particles [46]. We might assume that these shifts in binding energy are due to the charge transfer from Pd to Au atoms, which is indicative of alloy formation [19]. In other words, the noticeable negative shift in the Au 4f peak energy observed in our nanofibers is believed to be due to considerable clustering between Au and Pd atoms in the Pd-Au nano-sized particles in our TiO<sub>2</sub> fibers, which increase the opportunity for electron transfer from Pd to Au atoms [14, 47].



Figure 6. X-ray diffraction (XRD) peaks of Au/TiO<sub>2</sub>, Pd-Au/TiO<sub>2</sub>, and Pd/TiO<sub>2</sub>.

The powder X-ray diffraction (XRD) patterns of five different catalyst doped  $TiO_2$  fibers are shown in Figure 6. 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<sub>2</sub> 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(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 7. (A) N<sub>2</sub> adsorption-desorption isotherms and (B) BJH pore size distribution curves of Pd-Au/TiO<sub>2</sub> nanofibers.

The surface textural property of the fibers was further investigated by BET gas adsorption and desorption study. The  $N_2$  adsorption-desorption isotherms of the prepared Pd-Au/TiO<sub>2</sub>, Au/TiO<sub>2</sub>, and Pd/TiO<sub>2</sub> fibers, exhibited very similar profiles regarding classical type IV performance with a sharp capillary condensation step [48], indicating a well-defined H<sub>2</sub> 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<sub>2</sub> fibers (Figure 7B).

| Material  | $SSA^{a} (m^{2}/g)$ | Pore diameter <sup>b</sup> (nm) | Pore width <sup>c</sup> (nm) | Pore volume <sup>d</sup> (cm <sup>3</sup> /g) |
|---|---------------------|---------------------------------|------------------------------|---|
| Au/TiO <sub>2</sub>                               | 55.5                | 5.5                             | 6.1                          | 0.085   |
| Pd <sub>1</sub> Au <sub>2</sub> /TiO <sub>2</sub> | 72.5                | 4.3                             | 4.5                          | 0.078   |
| Pd <sub>1</sub> Au <sub>1</sub> /TiO <sub>2</sub> | 87.6                | 5.3                             | 6.1                          | 0.134   |
| Pd <sub>2</sub> Au <sub>1</sub> /TiO <sub>2</sub> | 103.3               | 4.8                             | 5.2                          | 0.132   |
| Pd/TiO <sub>2</sub>                               | 115.2               | 4.9                             | 5.5                          | 0.156   |

Table 2. Textural properties of Pd-Au/TiO<sub>2</sub>, Au/TiO<sub>2</sub>, and Pd/TiO<sub>2</sub> fibers.

<sup>a</sup>BET specific surface area, <sup>b</sup>BJH adsorption average pore diameter, <sup>c</sup>adsorption average pore width, <sup>d</sup>BJH adsorption cumulative volume of pores

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 7(B). All samples had majority of detected pore diameters in the size range of 2-12 nm. The corresponding surface area, pore size, and pore volumes of all fibers are summarized in Table 2. The BET surface areas of all the samples were between  $55-115 \text{ m}^2/\text{g}$ . It is interesting to note that the surface areas

and pore volumes increased with an increase of Pd content. These results show that the Pd/Au ratio is an important factor in controlling the final BET surface area and the uniformity of the dispersion of metal components without particle growth (Table 1) during the fabrication of Pd-Au doped  $TiO_2$  fibers, corresponding well with the above XRD and TEM analysis.



Figure 8. CO conversion (%) of Pd-Au doped TiO<sub>2</sub> fiber media.

The catalytic performances of Pd-Au/TiO<sub>2</sub> fiber media were evaluated and compared with that of Au/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> at a fixed-flow mixture gases of CO, oxygen, and helium. Figure 8 shows that CO oxidation on Au/TiO<sub>2</sub>, Pd<sub>1</sub>Au<sub>2</sub>/TiO<sub>2</sub>, Pd<sub>1</sub>Au<sub>1</sub>/TiO<sub>2</sub>, Pd<sub>2</sub>Au<sub>1</sub>/TiO<sub>2</sub>, Pd/TiO<sub>2</sub> initiated at approximately 150, 175, 125, 100, and 175°C respectively. Interestingly, under our experimental conditions, the Au/TiO<sub>2</sub> fiber media did not show any catalytic activity at reaction temperatures lower than 150°C. The possible cause might be size effect of gold particle. In comparison with other studies [49-50], Au particles sizes were approximately 20nm (Table 1). With an addition of Pd content, the catalytic activity was changed. Different particle compositions of Pd<sub>1</sub>Au<sub>2</sub>, and Pd<sub>1</sub>Au<sub>1</sub>/TiO<sub>2</sub> fiber media with about 4.8 wt% of metal loading, appeared to increase the catalytic activity and reduced the reaction temperature from 175°C for Pd<sub>1</sub>Au<sub>2</sub> to 125°C for Pd<sub>1</sub>Au<sub>1</sub>. Raising the Pd content of Pd<sub>2</sub>Au<sub>1</sub>/TiO<sub>2</sub> fiber medium induced a further reactivity increase and reduce the initial activity temperature to 100°C (as well as T10=125°C, T50=157°C). Complete (100%) CO conversion occurred at 200°C for Pd<sub>2</sub>Au<sub>1</sub>, which indicates a synergetic electronic ligand effect [5, 11]. It should be noted that the  $Pd_2Au_1$  catalyst doped TiO<sub>2</sub> fiber medium was the most active materials compared to other catalyst media.



Figure 9. (A) Turnover frequency (TOF) and (B) Arrhenius plots for CO oxidation.

By using the data reported in Figure 8 and Table 1, the corresponding turnover frequencies (TOF) were calculated and plotted in Figure 9(A). The Pd<sub>2</sub>Au<sub>1</sub>/TiO<sub>2</sub> fiber medium gave a TOF values of  $1.2 \times 10^{-1} \text{ s}^{-1}$  at 150°C, indicating significantly higher catalytic activity compared to both 2.5 x  $10^{-6} \text{ s}^{-1}$  of Pd/TiO<sub>2</sub> and 6.9 x  $10^{-5} \text{ s}^{-1}$  of Au/TiO<sub>2</sub> media. Furthermore, the TOF values of Pd<sub>2</sub>Au<sub>1</sub> were about a 5 times higher than that of the Pd<sub>1</sub>Au<sub>1</sub>. These data prove that the alloyed Pd-Au nanoparticle doped TiO<sub>2</sub> 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 the increase in reaction temperature to  $250^{\circ}$ C, TOF values of Pd<sub>2</sub>Au<sub>1</sub> increased to  $2.5 \times 10^{-1} \text{ s}^{-1}$  at 200°C. Whereas, TOF values of Au/TiO<sub>2</sub> was elevated to the highest value of  $4.6 \times 10^{-1} \text{ s}^{-1}$  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<sub>2</sub> medium above 250°C reaction temperature.

Figure 9(B) shows the linear Arrhenius plots [ln(TOF) vs 1/T] and the apparent activation energy (E<sub>a</sub>) of the CO oxidation over the five different Pd-Au particle composition. Interestingly, the activation energy of the Pd<sub>1</sub>Au<sub>1</sub>/TiO<sub>2</sub> medium was calculated to be 27.9 kJ/mol, which was the lowest value found among the catalyst studied. On the other hand, the steeper slopes observed with the mono-metal Pd/TiO<sub>2</sub> and Au/TiO<sub>2</sub> catalysts correspond to 84.9, and 61 kJ/mol. These values are similar to those reported in the literatures [11, 46].

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. These kinetic studies demonstrate that Au considerably enhanced the Pd catalytic activity over the composition range Pd:Au=1:1 (Pd<sub>52</sub>Au<sub>48</sub>) to Pd:Au=2:1 (Pd<sub>68</sub>Au<sub>32</sub>). These enhanced activities of Pd-Au/TiO<sub>2</sub> are attributed to the synergetic effect of Pd with the added Au and highly dispersed active components on the surface of the fibers [12], [18]. In other words, higher metal dispersion means higher exposed metal surface areas and consequently higher catalytic activity. Thus, the alloyed particle size may 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) [5, 12, 19, 51-52]. The average particle size and particle distribution was found to be 7.2 nm and 9.3 nm for Pd<sub>2</sub>Au<sub>1</sub> and Pd<sub>1</sub>Au<sub>1</sub> (Table 1) respectively. These two factors appear to have contributed significantly to the comparatively greater activity of the PdAu/ TiO<sub>2</sub> alloy than mono-metallic Pd/TiO<sub>2</sub> and Au/TiO<sub>2</sub> fiber supported catalysts.

The FTIR spectra of absorbed CO were used to identify the surface sites of the Pd-Au/TiO<sub>2</sub> fiber media. In Figure 10, all of the spectra showed appearance of bands indicative of CO in the gas phase (2169 and 2122 cm<sup>-1</sup>)[49]. For Pd<sub>2</sub>Au<sub>1</sub>/TiO<sub>2</sub> and Pd<sub>1</sub>Au<sub>1</sub>/TiO<sub>2</sub> fibers, the bands that appeared at approximately 2082 and 2077cm-1 were assigned to CO absorbed to the Pd-Au alloy structures, respectively. Increases in Au content reduces the multi-bonded CO by decreasing the Pd-Au nanoparticle size of the metal ensemble needed for multiple bonding [11], [54-55] and affect a small transfer of d electrons in the adsorbing palladium through the ligand effect [11], [56]. It could lead to the low frequency shift of the Pd<sub>1</sub>Au<sub>2</sub>/TiO<sub>2</sub> and Au/TiO<sub>2</sub> fiber materials that appeared at 2045 cm<sup>-1</sup> as shown in Figure 10.

### 4. Conclusion

In this work, submicron-sized Au/TiO<sub>2</sub>, Pd/TiO<sub>2</sub>, and Pd-Au/TiO<sub>2</sub> fibers were prepared by electrospinning, calcination of the polymer template fibers, and hydrazine reduction. The catalytic activities of these materials were tested systematically for CO oxidation. The fiber samples were characterized using 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 lower activity for Au/TiO<sub>2</sub> fiber medium was attributed to the large sizes of the gold particles. The smaller particle sizes achieved by the alloy Pd-Au nanoparticles (Pd<sub>2</sub>Au<sub>1</sub>/TiO<sub>2</sub> and Pd<sub>1</sub>Au<sub>1</sub>/TiO<sub>2</sub>) showed higher reactivity compared to monometallic Pd/TiO<sub>2</sub> and Au/TiO<sub>2</sub> fiber media. The enhanced reaction activity of Pd<sub>2</sub>Au<sub>1</sub>/TiO<sub>2</sub> fiber medium corresponded to higher activation energy and lower reaction temperatures.



**Figure 10.** 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  $O_2$ .

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