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Investigating the effect of gold-palladium bimetallic nanoparticles on TiO2 and the catalytic activity in CO oxidation

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Chapter 2

Experimental Section

2.1 Catalyst preparation

Several techniques have been developed to prepare supported gold nanoparticles. The following are some of the traditional methods used to synthesize supported gold nanoparticles for CO oxidation: Impregnation, cation exchange, co-precipitation and deposition-precipitation (DP) [1-3]. DP is the preferred method as it is believed to produce hemispherical gold metal particles with flat planes and also strongly attached to the support providing more surface area for reaction to occur [4]. In literature it has been reported that hemispherical gold metal can have strong metal-support interactions with some supports that are vital for the catalytic activity of gold catalysts. Haruta and co-workers reported that the gold catalysts prepared by DP method of size 2-3 nm were highly active for CO oxidation at room temperature [5-6].

DP involves a slow, uniform precipitation of gold onto a support while monitoring pH and temperature. The adsorption of gold species onto to the support is pH dependent and is determined according to the isoeletric point of the support (IEP) [7]. For an example a basic support such as TiO_2 will require pH adjustments in the range of 6-10 while such corrections are not applicable to acidic and hydrophobic supports such as SiO_2, WO_3, and SiO_2-Al_2O_3 [8]. Therefore monitoring pH during DP reaction is vital as it directly affects particle size. Haruta and co-workers found a positive relationship between pH and particle size [7]. Therefore choice of preparation method is crucial if nano particles of high monodispersity are ultimately to be synthesized.

In this study, the DP method has been adopted to synthesise supported gold catalysts as well as to attempt to produce bimetallic catalysts. The platinum group metal (PGM) incorporated is palladium. Both monometallic and bimetallic catalysts that were prepared were tested in a catalytic reaction for oxidizing CO.

2.1.1 Experimental materials

Both TiO_2 (P25 Degussa) and SiO_2 were used as support materials. The P25 was the standard mixture of 74% anatase and 26% rutile. Commercial $HAuCl_4$. $3H_2O$ and Pd $(NO_3)_2$. $2H_2O$ were used as precursors. Dilute aqueous NH_4OH was prepared from commercially available concentrated ammonia. The gases used for CO oxidation testing were 10% CO with a balance of He, 5% O_2 balance He and H_2. The gases used for catalysis were supplied by AFROX (African Oxygen) LTD.

2.1.2 Preparation of (Au/TiO_2)

The optimal synthesis conditions of monometallic gold catalysts were investigated through systematic variation of pH, weight percent Au, aging and calcination temperatures. The % loading of gold was the first study performed where the standard conditions were: pH 9, calcination temperature 200 °C, aging 72 h. Thereafter pH, calcination temperature and Aging were systematically studied. The various studies that were performed are given in Table 2.1

Table 2.1: The conditions studied for optimum preparation of supported gold catalysts

% Loading (Wt%)	**pH**	**Calcination Temperature C**	**Aging**
1[a]	7.5	200	2 h
3[a]	8	300	24 h
5[a]	9	400	72 h
8[a]	10	500	
10[a]			

[a] The standard synthesis conditions when % loading was varied: pH 9, calcination temperature 200 °C, aging 72 h

TiO_2 (2 g) support was suspended in a 200 ml distilled H_2O and heated up to 70 °C under vigorous stirring. Then pH was gradually increased from 3 to the desired pH by dropwise addition of NH_4OH (1M) solution before addition of Au solution. The gold precursor solution was then prepared by dissolving the nominal amounts of $HAuCl_4$ in 100 ml of distilled water. Thereafter, the gold solution was added dropwise under vigorous stirring to the aqueous suspension of titania while maintaining chosen pH with NH_4OH (1M) solution. The slurry was then aged to allow adsorption of gold nanoparticles.

After aging, all samples were filtered, washed with distilled water to remove chloride ions, and dried in an oven for 2 h at 120 °C. After drying, samples were calcined in air at the chosen temperature for 2 h. The powder samples were stored at room temperature in a desiccator under vacuum, away from direct sunlight light, in order to prevent any alteration [9].

The above procedure was also used to synthesize Au/SiO_2 catalysts.

2.1.3 Preparation of (Au-Pd/TiO_2)

The gold loading in the solutions corresponded to a nominal loading of 3 wt.% on the support and the nominal mass ratios of Au/Pd were 90:10, 75:25, 50:50, 25:50. A simultaneous deposition method was used to prepare the bimetallic catalysts, where by both the Au and Pd were mixed together as ions in a solution and deposited on the support (TiO_2 1g). The metals were deposited using NH_4OH solution. The suspension was stirred while maintaining pH 8 at 70 °C (during the titration). The wet samples were aged for 72 h to allow adsorption of small sized particles on the support.

The aged samples were filtered, washed with distilled water to remove chloride ions, and dried in an oven for 2 h at 120 °C. The dried samples were calcined at 200 °C then stored in a dessicator.

2.2 Characterization Techniques

The synthesized monometallic and bimetallic catalysts were characterized by transmission electron microscopy (TEM), high resolution transmission electron microscope (HRTEM), x-ray diffraction (XRD), temperature programmed desorption (TPD), inductively coupled plasma-optical emission spectrometer (ICP-OES), and surface area analysis using Brunauer Emmet and Teller (BET) apparatus.

2.2.1 TEM and HRTEM

High magnification TEM and HRTEM analysis were performed with an FEI Technai G2 spirit electron microscope and an FEI Tecnai F20 FEG TEM at 200kV. Samples for TEM analysis were prepared by sonication of catalysts in acetone for ~ 15 min and a few droplets of the resulting suspension were placed onto a holey carbon SPI copper grid. After leaving the grid to dry, it was then mounted onto the microscope holder. In addition to the images collected, energy-dispersive X-ray spectroscopy (EDS) spectra were also collected.

2.2.2 XRD analysis

The catalyst samples were analysed using a Bruker D5 Diffractometer. Powder samples were loaded on a sample holder and their diffraction patterns were recorded from 10 to 60 2θ and 40 to 50 2θ using CuKα radiation. The metals mean crystallite size (particle size) was calculated using PJF X-Ray Analyser software [10].

2.2.3 ICP-OES analysis

The gold content in the catalyst was determined by inductively coupled argon plasma emission spectroscopy (ICP-OES) on a Genesis ICP-OES Spectro instrument. The solid samples were digested in 5M concentrated HNO_3 solution.

2.2.4 Nitrogen Adsorption (BET) analysis

Nitrogen adsorption-desorption isotherms were measured on a Micromeritics TRISTAR 3000 analyzer. The samples were degassed under vacuum at 120 °C for 4 h before the nitrogen adsorption measurements. The specific surface areas were determined by the Brunauer-Emmett-Teller (BET) method.

2.2.5 TPD analysis

The CO-temperature programmed desorption experiments were performed in a U-shaped quartz tubular reactor charged with 0.1 g of the catalyst. The catalyst was degassed with helium flowing at 40 ml/min with temperature increasing to 150 ^{o}C at a rate of 10 ^{o}C/min and held at 150 ^{o}C for 1 h then cooled in helium. A mixture of carbon monoxide in helium (5%CO balance He) was passed over the catalyst for 1 h at 35 ^{o}C for the adsorption of CO on the surface/active sites of the sample. Desorption of CO was carried out under helium flowing at 40 ml/min while heating the sample from 35 to 800 ^{o}C at the rate of 10 ^{o}C/min. The CO-TPD profiles were obtained by measuring the amount of CO desorbed relative to the temperature, using a thermal conductivity detector.

2.3 Catalytic evaluation

The CO oxidation reactions were carried out in U-shaped quartz reactor. The temperature was measured by a thermocouple placed in the thermo-well (figure 2.1), which extended down to the catalyst bed. Before carrying out the measurements the system was calibrated with 10% CO and 5% O_2 gases balanced in helium. About 100 mg of the catalyst was loaded and pre-treated in H_2 for 1 hour at 150 ^oC. The reaction mixture consisted of 10% CO and 5% O_2 balanced by helium at a total flow rate of 40 ml/min. A GC equipped with a Porapak column and a thermal conductivity detector (TCD) was used to analyze the reaction products [11].

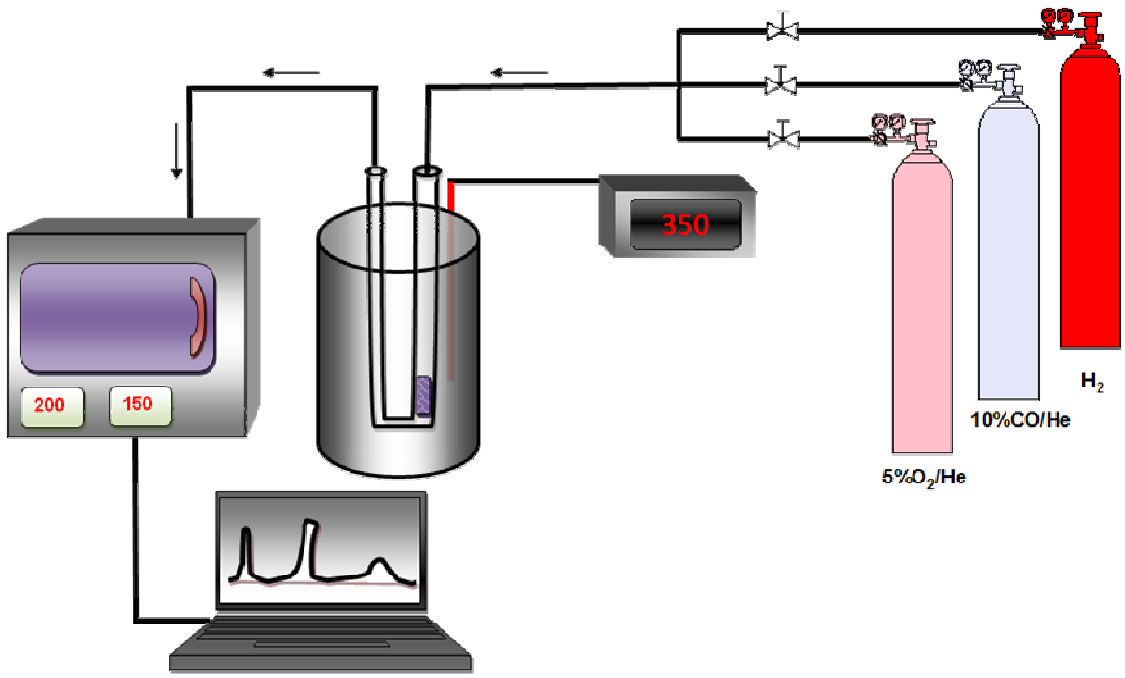


Figure 2.1: Schematic representation of the reactor used for CO oxidation

2.4 Calculations

The below equation (1) was used to calculate the percentage CO conversion of the catalyst after CO oxidation measurements were performed. The metal loading prior synthesis was calculated using equation (2).

$$\%CO \quad Conversion = \frac{CO_{(in)} - CO_{(out)}}{CO_{(in)}} \times 100\% \qquad (1)$$

$$Au \quad wt.\% = \frac{M_{(Au)}}{M_{(Au)} + M_{(Sup)}} \times 100\% \qquad (2)$$

Where: M: - is the molecular weight

Sup: - support

CO_{in} : - moles of carbon monoxide fed into the reactor

CO_{out} : - moles of carbon monoxide unreacted

2.5 References

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