Tanzania Journal of Science 48(2): 235-244, 2022
ISSN 0856-1761, e-ISSN 2507-7961

Carbon Monoxide Oxidation on Model Planar Titania Supported Platinum Nanoparticles Catalyst

Jovine Emmanuel[1*] and Brian Hayden[2]
[1]*Department of Chemistry, Mkwawa University College of Education,*
P.O. Box 2513, Iringa, Tanzania, E-mail: jovineemma2007@yahoo.co.uk
[2]*Department of Chemistry, University of Southampton, Southampton SO17 1BJ,*
United Kingdom, E-mail: beh@soton.ac.uk
**Corresponding author*

Received 4 Feb 2022, Revised 16 Apr 2022, Accepted 7 May 2022, Published Jun 2022
DOI: https://dx.doi.org/10.4314/tjs.v48i2.1

Abstract

A high-throughput (parallel) thermographic screening methodology was developed to enable the measurements of the particle size and support influence on heterogeneous catalysts. A high throughput screening chip has been used to establish the catalytic activity of titania supported platinum nanoparticles catalyst for CO oxidation reaction. The catalytic activity of Pt nanoparticles between 1.3 to 7.8 nm has been investigated for CO conversion at a pressure of 0.11 and 1.1 mbar with O_2:CO ratio of 1:1 at 80 °C and 0.6, 1.1 and 2.4 mbar at O_2:CO ratio of 1:1 at 240 °C. At these experimental conditions, there was an increase in the TOF with decreasing particle size for instance, at 80 °C and O_2:CO ratio of 1:1, total pressure of 0.11 and 1.1 mbar, the TOF increased from 0.01 s^{-1} to 0.171 s^{-1} with decreasing Pt particle size from 7.8 to 1.3 nm, respectively. However, Pt nanoparticles catalyst displayed higher activity at higher temperature, for example, the TOF increased from 3.312 s^{-1} to 4.355 s^{-1} at O_2:CO ratio of 1:1, total pressure of 0.6 and 1.1 mbar, respectively, for Pt particle size of 1.3 nm in agreement with the previous reports. Results show that CO oxidation on titania supported Pt nanoparticles catalyst is particle size dependent. On the other hand, findings from XPS measurements show no major change in the particle size after the reaction thus, reflecting the stability of Pt particles. While there is no apparent consensus in the literature reports on the activity trend with particle size for this system, these findings are consistent with most of the previously reported findings.

Keywords: platinum; titania; nanoparticles; thermography; CO oxidation.

Introduction

Catalysis is a phenomenon well known from ancient times in human history. It plays crucial roles in a wide range of applications including the chemical industries, pharmaceutical industries, energy conversion and environmental protection (Scheidtmann et al. 2001). The metal heterogeneous catalysts are largely dependent on support, morphology and size of the supported metal particles catalysts (Tsirlin 2002). Studies have shown that the activity of well characterised supported metal catalysts under similar reaction conditions is vital in knowing the effects of particle size and support (Tsirlin 2002). A good example of a heterogeneous catalyst exhibiting a strong support and particle size effect on activity is titania supported platinum in the low temperature oxidation of small molecules such as CO and hydrocarbons (Liu et al. 2010).

Platinum is one of the most useful and versatile heterogeneous metal catalysts which has been in use over many years. Its catalytic activity was reported back in the early 1800s when Dobereiner used it to catalyse the reaction of H_2 and O_2 in his portable lamp (Somorjai 1994). Platinum based catalysts are used in a number of reactions, including the conversion of aliphatic straight-chain hydrocarbons to aromatic molecules (dehydrocyclization) and branched molecules (isomerization) (Somorjai 1994). Platinum is also applied to large scale hydrogenation in chemical and petroleum-refining industries and ammonia oxidation, a crucial reaction step in the fertilizer production process (Somorjai 1994). More importantly, platinum is used for oxidation of carbon monoxide and unburned hydrocarbons in car emissions control (Franceschetti et al. 2003). Platinum catalyst is possibly the most commonly used and active electrode in fuel cell technology. Its stability both in oxidizing and reducing conditions has made it the best catalyst for many applications. Despite its enormous range of applications, platinum is a precious metal of high cost and low abundance, making its applications in different technologies more difficult (Cameron et al. 2003). Since platinum bear high cost, the priority has been its application at the atomic scale in heterogeneous catalysis. This involves the dispersion of platinum nanoparticles on stable high surface area metal oxide supports, such as Al_2O_3, TiO_2 and Fe_2O_3 thus, reducing the amount of platinum incorporated in the catalyst (Somorjai 1994). Supporting platinum catalysts, however, does not only lower the catalyst cost but also maximizes the active surface area of the catalyst and stabilizes the catalyst nanoparticles (Somorjai 1994). On the other hand, some supports, such as TiO_2, participate directly in the reaction mechanisms by activating the reactants and intermediates which in turn enhances the activity. Carbon supported platinum nanoparticles catalyst (Pt/C) is the most used catalyst in Polymer Electrolyte Membrane Fuel Cells (PEMFCs) technology in particular (Kim and Jhi 2011). However, the application of this catalyst system is hampered due to the loss of catalytic efficiency as a result of nanoparticle degradation, corrosion of cathode support and CO poisoning (Kim and Jhi 2011). The loss of efficiency occurs due to strong interaction of Pt with CO preventing oxygen from being adsorbed onto the catalyst surface (Schubert et al. 2001, Molina et al. 2009, Liu et al. 2010). Supported Pt catalysts are known as poor catalysts for CO oxidation at low temperature (Li et al. 2008). In order to overcome these shortcomings of carbon supported Pt, researchers have dedicated their efforts towards looking for more efficient Pt nanoparticle catalyst supports to combat the effects of catalyst degradation, corrosion and high temperature reaction catalysis.

Over the last decade, Fe_2O_3 supported Pt nanoparticles catalyst has shown unusual high catalytic behaviour for CO oxidation at low temperature (Liu et al. 2010). The activity is attributed to the capability of Fe_2O_3 to supply active oxygen during the reaction. Studies indicate that CO oxidation reactions on titania supported Pt particles below 5 nm either display low activity or show no strong size dependence (Rashkeev et al. 2007). Theoretical calculations suggest that Pt particles of 1 or 2 nm sizes are more active for CO oxidation (Dobrin 2012). Studies have also shown that Pt particles of 2 nm size are the most active for CO oxidation compared to 3 nm and 5 nm sizes (Kageyama et al. 2013). Whereas the combinatorial synthesis of well characterised model oxide supported metal particle electrocatalysts allowed the screening of a number of electrochemical reactions on various supports using a high-throughput electrochemical chip, the application of a high-throughput screen for heterogeneous catalyst reaction is challenging. A graceful approach suitable for thin film low area alloy catalysts has been revealed for H_2-D_2 exchange reaction employing a 100 channel microreactor array and mass spectroscopy (Emmanuel et al. 2019). For simple reactions in which it is less important to determine selectivity, net activity determined in an exothermic reaction using high-throughput infrared thermography technique is promising. This has been realised for the screening of catalysts in the oxidation of hydrogen and octane on high area catalyst samples (Emmanuel et al. 2019). However, the extension of the technique to arrays of well characterised model catalysts such as metal supported electro-catalysts to obtain structure/activity relationships is still a challenge (Hayden 2013). The considerably lower surface areas of these planar catalysts require an amplified sensitivity in order to identify the heat generated in the course of a reaction. This study reports the application of a nano-fabricated substrate which enables the high-throughput measurement of titania supported platinum catalysts where the particle size has been controlled, enabling the particle size dependence of the reaction to be measured concurrently in a similar gas phase setting.

Materials and Methods

Synthesis of platinum nanoparticles catalyst

A high-throughput combinatorial method based on a high throughput physical vapour deposition (HT-PVD) described elsewhere (Guerin and Hayden 2006) was used to synthesise both thin films of TiO_2 and TiO_2 supported platinum nanoparticles catalyst. This method deposits thin films by condensation of a vaporized material onto a substrate. The deposition chamber consisted of three electron gun (e-gun) evaporation sources (Temescal) and three Knudsen cell (K-cell) sources (DCA). The HT-PVD system operational base pressure was 1×10^{-10} mbar. In this study, electron beam sources, E-gun 1 was used to evaporate Ti and Pt was evaporated from E-gun 3. Titania layers of approximately 200 nm were deposited onto a catalyst screening chip from titanium (99.995%, Alfa Aesar metals) from E-gun 1 and oxygen (Air products, special gases, 99.999%) at a constant pressure of 9.7×10^{-6} Torr at 1 sccm oxygen flow rate and plasma source, P_{rf} = 300 W at a deposition rate of 4 Å/s with substrate kept at room temperature during film synthesis. The thicknesses of titania layer deposits were controlled through deposition time and sample thickness was subsequently established by calibration of deposition rates from Atomic Force Microscope (AFM) measurements. The AFM (Vecco Autoprobe M5) instrument was used in a contact mode with a silicon cantilever, resonance frequency of 180 kHz, spring constant of 5 Nm^{-1} with an approximate tip (CSC17 probe, MikroMasch) of 10 nm curvature.

Platinum nanoparticles characterisation

For particle size characterisation and distribution using Transmission Electron Microscope (TEM), a thin layer of titanium dioxide, 15–25 nm thick, was deposited onto small carbon coated copper TEM grids (Agar Scientific). These grids had TiO_2 deposited under similar deposition conditions as on a catalyst screening chip. The platinum particles from platinum source (E-gun 3), were deposited onto a screening chip on which a titanium dioxide support material had been previously grown using a HT-PVD method. The deposition rate of 4 Å/s were established by depositing several thick layers from short to longer times, to ensure that the thickness as established on contact masked samples by AFM was relative to the deposition time. The rate of platinum deposition (0.15 Å/s) was determined with the synthesis of continuous platinum thin films and short deposition times (30–360 s) were used to produce the Pt particles through nucleation and growth on the titania substrates at ca. 200 °C; this temperature has been reported to produce stable particles (Zhang et al. 1997). For surface characterisation of platinum particles on the titania layer, platinum particles were deposited onto Formvar® carbon coated copper grids (Agar Scientific) that had been coated with a thin layer of titania, 15–25 nm thick, for TEM analysis. Particle characterisation was carried out using TEM before deposition onto the screening chip to ensure that particles were being synthesised. The TEM images were acquired using a Jeol 3010 instrument at an accelerating voltage of 300 kV incorporating a Gatan CCD camera for recording the images. Particles were deposited at the rate of 0.15 Å/s and the substrate deposition temperature was 200 °C. X-ray Photoectron Spectroscope (XPS) measurements were undertaken in Ultra High Vacuum (UHV) system incorporating a twin anode X-ray source (Mg Kα and Al Kα), and a VG Clam Single Channel XPS system analyser. The depositions were carried out onto silicon nitride on silicon and on a 10 × 10 or 12 × 12 array nano-fabricated catalyst screening chip (450 µm silicon wafer thickness) on which a low pressure chemical vapour deposited (LP-CVD) silicon nitride membrane (300 nm or 600 nm) had been deposited. The screening chip had been back etched to produce individual membranes. The HT-PVD system was set up on a "wedge" deposition in order to produce various particle sizes distributions across the substrate.

A silicon screening chip with an overall dimension of 35 mm × 35 mm was fabricated (450 mm thick silicon wafer) for the high throughput infrared thermography measurements and an array of 10 × 10 or 12 × 12 silicon nitride membranes (1.5 mm × 1.5 mm) of thickness 600 nm were created by back etching the silicon to a layer of LP-CVD silicon nitride as earlier described (Emmanuel et al. 2019). The membrane with the 200 nm of titania supported catalyst was optically transparent. For the measurement of temperature of the membrane, a thin graphitic carbon layer (ca. 200 nm) was deposited on the back of the membrane providing an emissivity close to that of a black body. The goal of a thin SiN membrane was to offer a support for the catalyst which had a small thermal mass and minimal thermal conductivity to the surrounding silicon chip thus; heat generated during reaction on the catalyst would consequently raise the temperature of the membrane.

Screening of platinum catalyst for catalytic activity

The screening chip with the catalyst synthesized over the complete chip was mounted on a heated sample holder with a heat shield which could allow the complete chip to be heated homogeneously to a reaction base temperature of up to ca. 250 °C as previously reported (Emmanuel et al. 2019). This means that SiN membrane on which Pt nanoparticles and titania support were grown had the ability to withstand the temperature of up to 250 °C. The sample holder was mounted in a UHV chamber incorporating an IR transparent window (CaF_2) and the surface of the chip imaged (50 mm focal length camera lens) using a thermal camera (Jade III, CEDIP) operating in the spectral range of 3.6–5.1 µm with a thermal sensitivity of ca. 20 mK. The spatial resolution of the camera was 320 × 240 pixels, and the complete 10 × 10 array was imaged to fill the detector. The reactions were carried out in a turbomolecular pumped UHV chamber with a base pressure of 1×10^{-10} mbar and the total pressure of the gas mixture was 0.11 and 1.1 mbar at O_2:CO ratio of 1:1 at 80 °C and 0.6, 1.1 and 2.4 mbar at O_2:CO ratio of 1:1 at 240 °C. The temperature response of the catalyst on the membrane for a given power input (from an exohermic reaction) was calculated through finite element thermal modelling (Comsol Multiphisics®) (Emmanuel et al. 2019). The assumption was that the energy loss over the membrane would be due to conduction through the membrane (together with the titania support and the graphite layer) to the supporting silicon chip. Radiative and convective losses were assumed to be zero thus, additional radiative and convective losses over a few degrees temperature over the base temperature of reaction would be expected to be very small (Emmanuel et al. 2019). For CO oxidation reaction ($\Delta H = -283$ $kJmol^{-1}$) for a pressure of 1×10^{-3} mbar, assuming every molecule reacts, the theoretical power was 2.289×10^{-4} Js^{-1} mm^{-2}. This leads in a calculated temperature rise at the centre of the membrane, $\Delta T = 4$ °C. The calculated sensitivity of the chip was used to calculate the TOF of reaction at the surface: the errors associated with the absolute value of the TOF were estimated to be ca. +/- 30% mainly because of uncertainties in the thermal conductivity values for the membrane composite layer. A simulation of the temperature distribution across the 1.5 mm × 1.5 mm membrane had been previously reported (Emmanuel et al. 2019) which has been applied here to study a different catalyst system.

Results and Discussion

TEM images of platinum catalyst supported on titania resemble those obtained previously in high throughput electrocatalytic measurements of the same catalyst system (Hayden et al. 2009). The similarity with the ones reported earlier is in terms of particle growth on the substrates with the deposition time where by particles grew in size as the deposition time increased taking hemispherical shape. TEM images of titania supported Pt catalyst are presented in Figure 1. It is seen in Figure 1 that, in (a) Pt particles are smaller (black) clusters because less Pt is deposited at shorter deposition time (30 seconds). As the deposition time increases, the Pt particles grow in size because more Pt is deposited and this is reflected in the size of the particles in (d) whose deposition time is 5 minutes.

TEM images were used to acquire the particle size dependence of supported platinum as a function of the equivalent coverage of platinum deposited. Nucleation and growth results for particle size distributions for three equivalent coverages of platinum are shown in Figure 2.

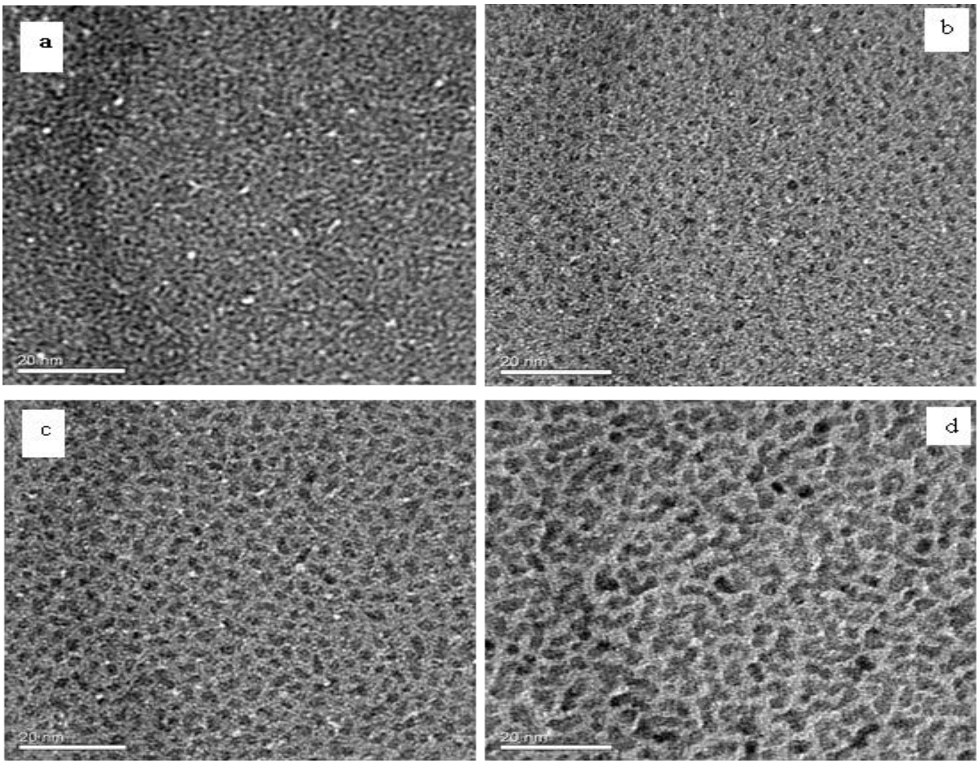

Figure 1: TEM images of Pt nanoparticles supported on titania for the four different deposition times, (a) 0.5 min, (b) 2 min, (c) 3.5 min and (d) 5 min corresponding to mean particle sizes of (a) 1.6 nm, (b) 2.6 nm, (c) 4.9 nm and (d) 6.7 nm.

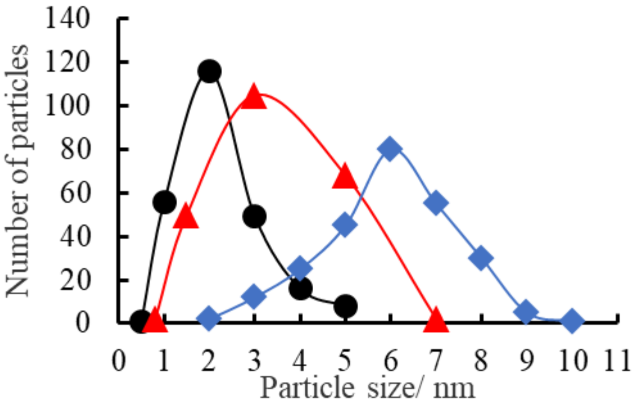

Figure 2: Platinum nanoparticle size distributions at various deposition times at a deposition rate of 0.15 Ås^{-1} determined for three equivalent thicknesses of platinum from TEM images: circles 1.6 Å (30 s), triangles 26 Å (120 s), squares 67 Å (300 s).

TEM and XPS studies were undertaken before and after the reaction in order to establish whether there was a major change in the particle size distribution after CO oxidation reaction because it was not possible to establish the distributions right on the screening chip. Figure 3 indicates the dependence of Pt $4f_{7/2}$ binding energy as a function of the platinum particle size measured both before and after the reaction on the platinum supported catalysts on the screening chip. A small change in binding energy shift (0.9 eV) was observed, implying that the particles remained stable throughout the reaction conditions. Increase in the intensity was observed with increasing particle size, which indicates that Pt particles were growing in size as more Pt was deposited with deposition time. The measurements were made before and after CO oxidation reaction had taken place at 80 °C and 240 °C. Within experimental error, the binding energy of platinum remained the same for each particle size, indicating that there was a small change in particle size during the reaction. The measurements were made before (red points) and after (black points) the CO oxidation reaction had taken place.

During the experiment, the total pressure of the gas mixture was 0.11 mbar and 1.1 mbar at O_2:CO ratio of 1:1 at 80 °C and 0.6 mbar, 1.1 mbar and 2.4 mbar at O_2:CO ratio of 1:1 at 240 °C and the temperature was measured concurrently on all the catalysts over a 5 minutes interval. The change in temperature across a row of the same particle sizes was ca. 0.2 °C, far smaller than the changes in the columns and could be associated with a partial shielding of the gas flux at the edges of the sample by the holder. The temperature rise ΔT in average assisted the computation of the conversion rate of CO to CO_2 at the catalyst assuming the enthalpy of reaction was $\Delta H = -283$ kJ mol^{-1} (Emmanuel et al. 2019). The mass of platinum and the number of platinum atoms at the surface of the particles per area of catalyst was computed from the TEM images, assuming the particles were hemispherical (Hayden et al. 2009, Emmanuel et al. 2019). This allowed the computation of the turn over frequency (TOF) at the Pt surface. Figure 4 is a plot of the TOF for CO oxidation reaction at 80 °C with the total pressure of 0.11 and 1.1 mbar at O_2:CO ratio of 1:1. At these reaction conditions, a monotonic increase in the TOF with decreasing particle size was observed. Figure 5 is a plot of the TOF for CO oxidation reaction at 240 °C with total pressures of 0.6, 1.1 and 2.4 mbar at O_2:CO ratio of 1:1. Yet again, under these reaction conditions, a monotonic increase in the TOF with decreasing particle size was observed.

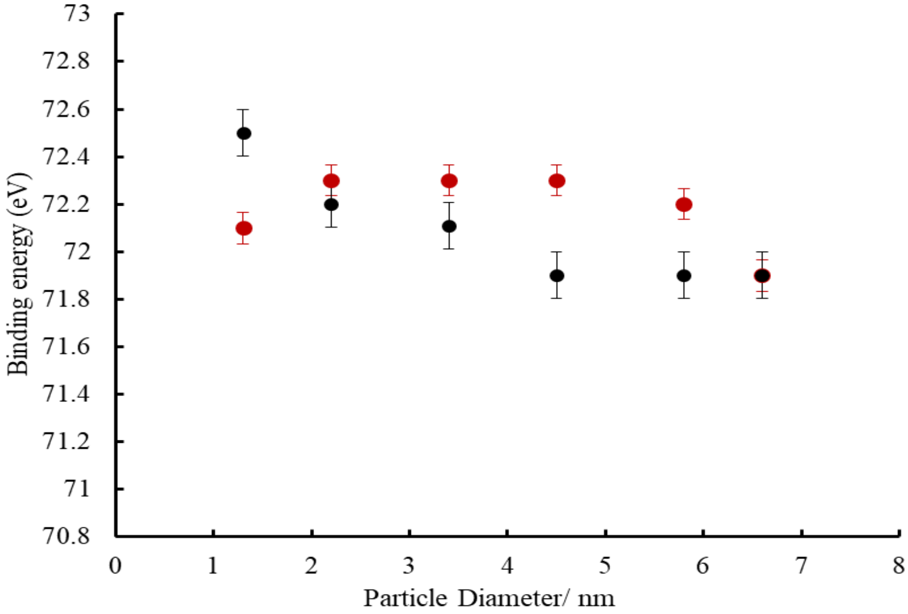

Figure 3: The Pt $4f_{7/2}$ binding energy measured by XPS for the titania supported platinum particles as a function of particle size.

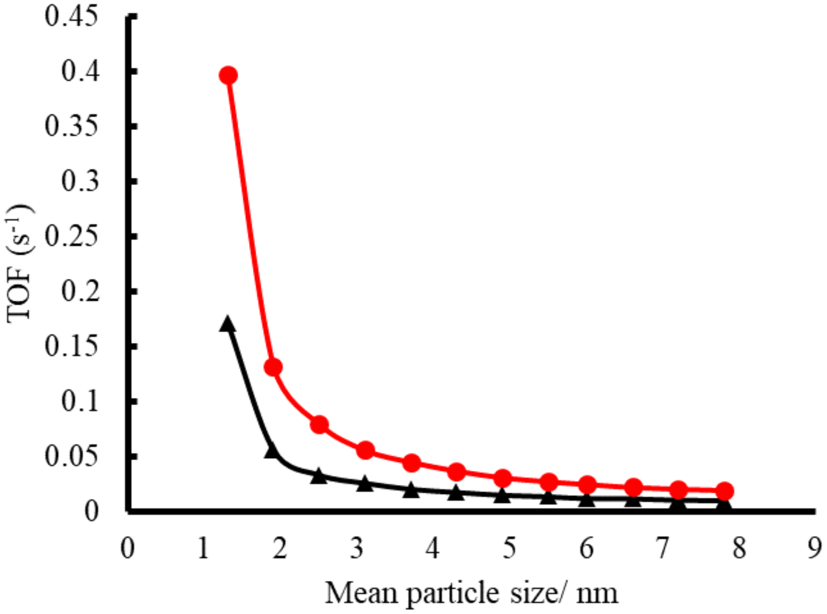

Figure 4: The TOF for the CO oxidation reaction on titania supported platinum particles at 80 °C and a O_2:CO ratio of 1:1. Results are shown for the total pressures of 0.11 mbar (black triangles) and 1.1 mbar (red circles).

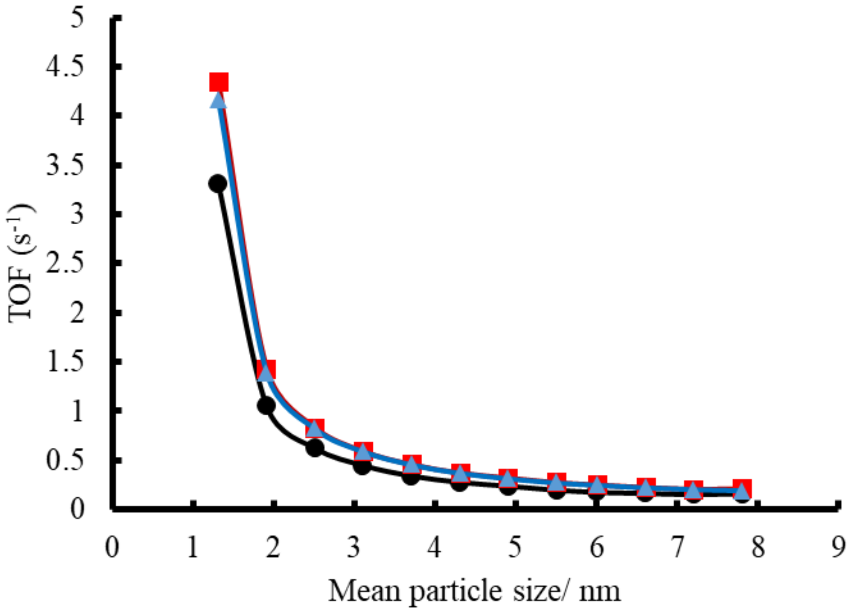

Figure 5: The TOF for the CO oxidation reaction on titania supported platinum particles at 240 °C and O_2:CO ratio of 1:1. Results are shown for total pressures of 0.6 mbar (black circles), 1.1 mbar (red squares) and 2.4 mbar (blue triangles).

At all these reaction conditions studied, the TOF clearly showed that the CO oxidation reaction on supported Pt catalysts is particle size dependent with the TOF increasing with decreasing particle size. The activity trend seen in this study is inconsistent with the previous reports that either the activity for CO oxidation on Pt particles smaller than 5 nm supported on titania decreases with decreasing Pt particle size or shows no strong size dependence (Bamwenda et al. 1997, Haruta 2003, Rashkeev et al. 2007) . However, the monotonic increase in the TOF for CO oxidation on titania supported Pt observed was consistent with observations made in earlier studies that the activity of high area titania supported Pt catalysts in the range between 1.1 nm 10 nm diameter particles increases with decreasing particle sizes (Li et al. 2013). Studies revealed that for CO oxidation reaction at a particular reaction temperature, the activity increases with decreasing particle sizes (Bamwenda et al. 1997, Li et al. 2013). For instance, at 80 °C and O_2:CO ratio of 1:1, total pressure of 0.11 and 1.1 mbar (Figure 4), the TOF increased from 0.01 s^{-1} to 0.171 s^{-1} with decreasing Pt particle size from 7.8 to 1.3 nm, respectively, an increase in activity by a factor of 17. For the Pt particle sizes investigated in this study, there was no decline in activity with decreasing particle size. However, an increase in the rate was observed as the reaction temperature was increased for a particular particle size and gas pressure. Higher rate of Pt activity was observed at elevated temperatures (Figure 5). For instance, there was an increase in the TOF from 3.312 s^{-1} to 4.355 s^{-1} at O_2:CO ratio of 1:1 and a total pressure of 0.6 and 1.1 mbar, respectively, for Pt particle size of 1.3 nm. It has been observed that CO oxidation on Pt at higher temperature results in higher rate compared to that recorded at relatively low temperatures. The increase in the rate observed here with decreasing particle size is proportional to the Pt particles diameter (curves fitted to data in Figures 4 and 5).

These results are consistent with the previous reports on titania supported platinum catalyst that suggest the participation of the substrate to account for the low temperature CO oxidation activity of titania supported platinum among other factors (Li et al. 2008). The findings indicate that the type of support changes the activity of supported Pt towards CO oxidation. Platinum supported on TiO_2 is the most active catalyst for CO oxidation compared to other supports (Alexeev et al. 2005). Generally, studies have shown that CO oxidation reaction on titania supported Pt nanoparticles of the size ranging between 2 and 5 nm demonstrated high activity for CO conversion in the temperature range between 60 to 140 °C (Kageyama et al. 2013). However, Pt nanoparticles of 2 nm size displayed the highest CO conversion at 60 °C (Kageyama et al. 2013). Theoretical results on CO oxidation reaction on Pt particles containing 55-atom cluster (1.1 nm) and 147-atoms cluster (1.6 nm) suggested that Pt particles of around 2 nm size would be the most efficient in CO oxidation compared to particles of 1.1 nm size or less (Dobrin 2012). The findings indicated that larger clusters such as 147-atom cluster contain high coordinated CO adsorption sites on the Pt (111) and Pt (100) faces supplemented by the presence of adjacent low-coordinated oxygen adsorption sites on the edges of the cluster. Though these results are of smaller Pt particles than the ones investigated in this study, they serve to illustrate the strong particle size dependence for CO oxidation on Pt particles. Studies of CO oxidation on supported platinum nano-particles provide evidence that titania supported platinum with similar range of particle sizes shows high activity while silica supported platinum is much less active confirming the participation of titania in the reaction (Li et al. 2013).

Conclusion

The catalytic activity of titania supported Pt nanoparticles ranging between 1.3 and 7.8 nm has been investigated for CO oxidation. At the experimental conditions studied, a monotonic increase in the TOF was observed with decreasing Pt particle size. For instance, the TOF increased from 0.01 s^{-1} to 0.171 s^{-1} with decreasing Pt particle size from 7.8 to 1.3 nm, respectively, at 80 °C and O_2:CO ratio of 1:1, total pressure of 0.11 and 1.1 mbar. However, Pt nanoparticles displayed the highest activity at higher temperature in agreement with previous reports on the same catalyst system. Results from XPS measurements indicated that there was no major change in the particle size after the reaction which reflects the stability of Pt particles. Therefore, results indicate that CO oxidation on titania supported Pt nanoparticles catalyst is particle size dependent. While there is no actual consensus in the literature concerning the particle size effect for this system, this result is in good agreement with findings on high area supported catalysts, reporting a seven-fold increase in activity for particles between 1 nm and 10 nm sizes.

Declaration of Competing Interest: No conflicts of interest to declare.

Acknowledgement

The authors honourably acknowledge Mkwawa University College of Education for financial support for this study.

References

Alexeev OS, Chin SY, Engelhard MH, Ortiz-Soto L and Amiridis MD 2005 Effects of reduction temperature and metal-support interactions on the catalytic activity Pt/gamma-Al_2O_3 and Pt/TiO_2 for the oxidation of CO in the presence and absence of H_2. *J. Phys Chem. B* 109(49): 23430-23443.

Bamwenda GR, Tsubota S, Nakamura T and Haruta M 1997 The influence of the preparation methods on the catalytic activity of platinum and gold supported on TiO_2 for CO oxidation. *Catal. Lett.* 44(1-2): 83-87.

Cameron D, Holliday R and Thompson D 2003 Gold's future role in fuel cell systems. *J. Power Sources* 118(1-2): 298-303

Dobrin S 2012 CO oxidation on Pt nanoclusters, size and coverage effects: a density functional theory study *Phys. Chem. Chem. Phys* 14(35): 12122-12129.

Emmanuel J, Hayden BE and Saleh-Subaie J 2019 The particle size dependence of CO oxidation on model planar titania supported gold catalysts measured by parallel thermographic imaging. *J. Catal.* 369: 175-180.

Franceschetti A, Pennycook SJ and Pantelides ST 2003 Oxygen chemisorption on Au nanoparticles. *Chem. Phys. Lett.* 374(5-6): 471-475.

Guerin S and Hayden BE 2006 Physical vapor deposition method for the high-throughput synthesis of solid-state material libraries. *J. Comb. Chem.* 8(1): 66-73.

Haruta M 2003 When gold is not noble: Catalysis by nanoparticles. *Chem. Rec* 3(2): 75-87.

Hayden BE 2013 Particle size and support effects in electrocatalysis. *Acc.Chem. Res.* 46(8): 1858-1866.

Hayden BE, Pletcher D, Suchsland JP and Williams LJ 2009 The influence of Pt particle size on the surface oxidation of titania supported platinum. *Phys. Chem. Phys.* 11(10): 1564-1570.

Kageyama S, Sugano Y, Hamaguchi Y, Kugai J, Ohkubo Y, Seino S, Nakagawa T, Ichikawa S and Yamamoto TA 2013 Pt/TiO_2 composite nanoparticles synthesized by electron beam irradiation for preferential CO oxidation. *Mater. Res. Bull.* 48(4): 1347-1351.

Kim G and Jhi SH 2011 Carbon monoxide-tolerant platinum nanoparticle catalysts on defect-engineered graphene. *Acs Nano* 5(2): 805-810.

Li N, Chen QY, Luo LF, Huang WX, Luo MF, Hu GS and Lu JQ 2013 Kinetic study and the effect of particle size on low temperature CO oxidation over Pt/TiO_2 catalysts. *Appl. Catal. B-Environ.*142: 523-532.

Li S, Liu G, Lian H, Jia M, Zhao G, Jiang D and Zhang W 2008 Low-temperature CO oxidation over supported Pt catalysts prepared by colloid-deposition method. *Catal. Commun.* 9(6): 1045-1049.

Liu L, Zhou F, Wang L, Qi X, Shi F and Deng Y 2010 Low-temperature CO oxidation over supported Pt, Pd catalysts: Particular role of FeOx support for oxygen supply during reactions. *J. Catal.* 274(1): 1-10.

Molina LM, Lesarri A and Alonso JA 2009 New insights on the reaction mechanisms for CO oxidation on Au catalysts. *Chem. Phys. Lett.* 468(4-6): 201-204.

Rashkeev SN, Lupini AR, Overbury SH, Pennycook SJ and Pantelides ST 2007 Role of the nanoscale in catalytic CO oxidation by supported Au and Pt nanostructures. *Phys. Rev. B* 76(3): 035438-8

Scheidtmann J, Weib PA and Maier WF 2001 Hunting for better catalysts and materials-combinatorial chemistry and high throughput technology. *Appl. Catal. A-Gen.* 222(1-2): 79-89.

Schubert MM, Hackenberg S, Van Veen AC, Muhler M, Plzak V and Behm RJ 2001 CO oxidation over supported gold catalysts-"inert" and "active" support materials and their role for the oxygen supply during reaction. *J. Catal.* 197(1): 113-122.

Somorjai GA 1994 Introduction to Surface Chemistry and Catalysis. John Wiley & Sons.

Tsirlin T, Zhu J, Grunes J and Somorjai GA 2002 AFM and TEM studies of Pt nanoparticle arrays supported on alumina model catalyst prepared by electron beam lithography. *Top. Catal*. 19(2): 165-170.

Zhang L, Persaud R, and Madey TE 1997 Ultrathin metal films on a metal oxide surface: Growth of Au on TiO_2 (110). *Phys. Rev. B* 56(16): 10549-10557.