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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 4

Catalytic oxidation CO over Au-Pd/TiO_2

4.1 Introduction

Though CO is not really classified as greenhouse gas it is produced during the process of burning coal and is toxic and hence more lethal than CO_2. It mainly results from an incomplete combustion of carbon and carbon-containing compounds [1]. It is a colorless, odorless, poisonous gas when inhaled it combines with haemoglobin to form carboxyhaemoglobin, reducing the oxygen-carrying ability of the blood. This gas in not only harmful to human beings but it also hampers the functioning of fuel cells. It has been demonstrated that it inhibits the functioning of platinum electrode in a fuel cell which is known to be sensitive to carbon monoxide poisoning [2-3]. The selective catalytic carbon monoxide oxidation has been proposed as the most promising way of removing carbon monoxide [4]. The low temperature CO oxidation catalysts are used in residential and automotive air cleaning technologies, gas masks for mining applications, CO detectors, and selective oxidation of CO in reformer gas for fuel cell applications [1].

In heterogenous catalysis CO oxidation is a well known reaction that can be catalyzed by various catalysts. Platinum group metals have been earlier reported as catalysts for this reaction. The frequent use of platinum supported catalysts has been reported in the literature [5]. However, it was reported that high CO concentration leads to poisoning of platinum catalysts which leads to deactivation [6]. Therefore it has been predicted that the Pt-Pd alloys in three-way catalyst (TWC) for diesel oxidation catalyst (DOC) will experience rapid deactivation at high temperatures caused by large particle aggregates [6]. The hopcalite catalysts (mixed oxides composed mainly of Mn and Cu) have also been reported but they are easily deactivated at ambient temperatures [1]. The pioneering work of Haruta showed that the supported Au catalysts have high activity for CO oxidation particularly at ambient temperature [7]. However, it was later discovered that these catalysts rapidly deactivate at high temperatures due to sintering of the gold [7]. The lack of thermal stability of these catalysts hinders its applications particularly for high temperature systems. Due to the greater availability and stability of the price of gold compared to the platinum group metals (PGMs),

it is important that the activity of gold catalysts is optimized [8]. Therefore manipulation or modification of these catalysts is required for improved activity and stability.

The Au/Pd system has been extensively studied [9-12]. While the two metals are said to be immiscible, Pd metal has a great thermal stability. The potential great thermal stability introduced by Pd metal makes Au/Pd system ideal for operating in high temperature systems and hence desirable to produce. Au-Pd catalysts are ideal for operating in cars that run on petrol. For example when the car starts the engine is cooler, the reactions taking place in the catalytic converter will occur on the active sites of Au. At high temperatures, the reaction will occur on both Pd and Au active sites. The Pd metal will provide thermal stability preventing particle sintering of gold thus Au will operate under such conditions.

To assess the applicability of the catalysts produced as described in Chapter 3, we report on CO oxidation over Au/TiO_2 and $Au-Pd/TiO_2$ catalysts. The preliminary results in Chapter 3 showed that the $Au-Pd/TiO_2$ catalysts synthesized via deposition-precipitation method have both Au and Pd metals individually attached on the support. Therefore they show a heterostructred bimetallic system.

4.2 Catalytic measurements

The CO oxidation reactions were carried out in a U-shaped quartz reactor. Before carrying out measurements the catalysts (0.1 g) were pretreated in hydrogen for 1 h at 150 ^{o}C. Thereafter the 10%CO and 5% O_2 gases balanced by helium were set to flow at 40 ml/min and the reaction was left to run for 12 h. A GC equipped with a thermal conductivity detector (TCD) was used to analyze the reaction.

4.3 Results and discussion

4.3.1 Temperature studies of Au/TiO_2

The results on the effect of reaction temperature on the catalytic activity of CO oxidation over of Au/TiO_2 catalyst are presented in Fig 4.1 below. Prior catalytic measurements the catalysts were pretreated in hydrogen at 150 °C for 1 h to ensure full reduction of gold

particles to their metallic state. The hydrogen pretreatment was necessary for activating the catalysts as the used catalysts were not freshly prepared. Haruta et al. demonstrated that CO and O_2 can easily adsorb on Au surfaces at room temperature after pretreatment [13]. Other researchers reported that catalytic activity of Au/Al_2O_3 could be restored by hydrogen or water treatment [15-16]. Ntho also showed that hydrogen pretreatment enhanced the activity of Au/TiO_2 catalyst compared with oxygen pretreatment [16].

To ensure full adsorption of CO and O_2 onto the active sites, both CO and O_2 gases were allowed to flow into the reactor for 1 h at the desired reaction temperature.

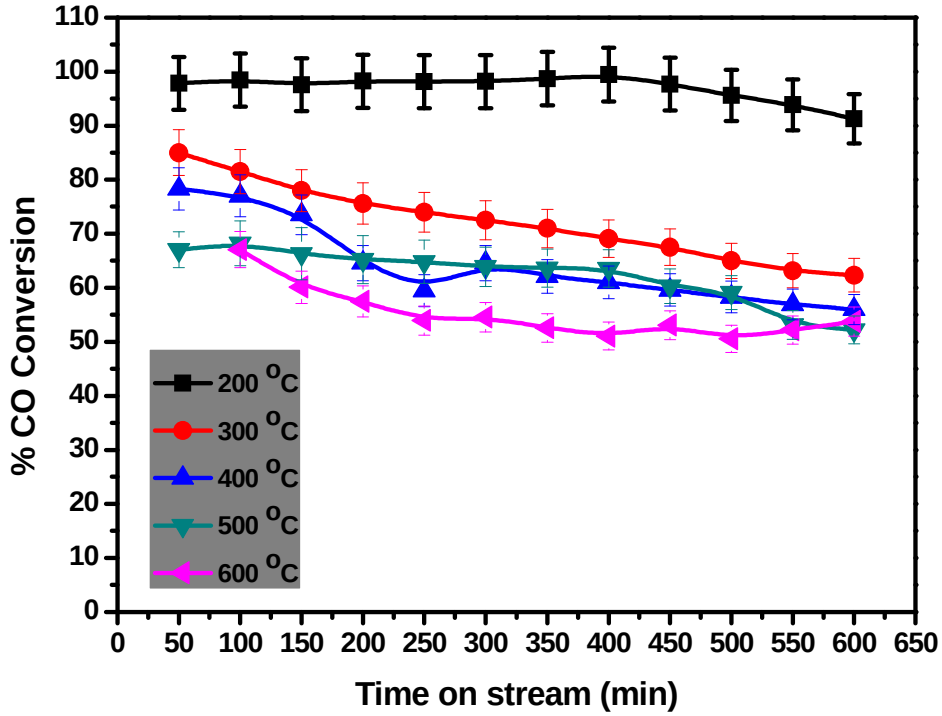


Figure 4.1: CO oxidation activity as a function of time on stream on Au-TiO_2 (3% Au loading) catalyst at various temperatures.

It is observed in Fig 4.1 that at 200 °C the CO conversion was almost 100 %. It is also seen that as the initial CO conversion at 50 min decreases with increasing reaction temperature. It is observed that catalysts activity decline rapidly with time on stream, especially for 300 and 400 °C. After 600 min the observed conversion of 300 and 400 °C is 62% and 56% respectively. The rapid deactivation observed could be attributed to loss of surface area that occurs when Au particles agglomerate forming large particle aggregates [2]. Sintering of Au particles is attributed to low melting point resulting from reduced dimensions of Au [17]. Formation of bicarbonate species formed from the CO_2 produced during CO oxidation reaction has been reported [19]. These bicarbonates species have been reported as possible

reaction intermediates during CO oxidation [18]. Kim and Thompson reported the formation bicarbonates and formate species that further act as competitive intermediates for active sites. The decrease in catalytic activity of CO oxidation at high reaction temperature can be assigned to blockage of active sites occupied by carbonates and formate species [19]. The decrease in activity indicates the short term stability of the catalysts. Daté and co-workers reported aging and storing conditions as some of the factors that contribute to the instability and short lifetime of the Au catalysts [19].

It is also observed that the activity of the catalyst at 500 °C decreases with CO conversion to 52%. There is no conversion observed for the catalyst at 600 °C for the first 50 min, which could be due to the decreased amount of active sites. Tsubota et al. reveal that for Au/TiO_2 catalysts calcined at 300 °C and above there were no Au^+ species present [20]. Therefore metallic Au species are the only available active sites [20]. There is steady conversion observed at 600 °C after 50 min which could be due to the reaction occurring at metallic Au active sites. It is also observed that activity tend to decrease with increasing time on stream. The activity dependency of Au catalyst on particles size was reported as early as 1970 by Cha and Parravano [21]. A large number of studies conducted suggest that metallic Au is important, particularly small sized Au metal particles are necessary [22-23]. Other authors claimed that activity increases with the amount of active species available [24].

The CO-TPD profile (Fig 4.3) was obtained by measuring the amount of CO desorbed relative to the temperature.

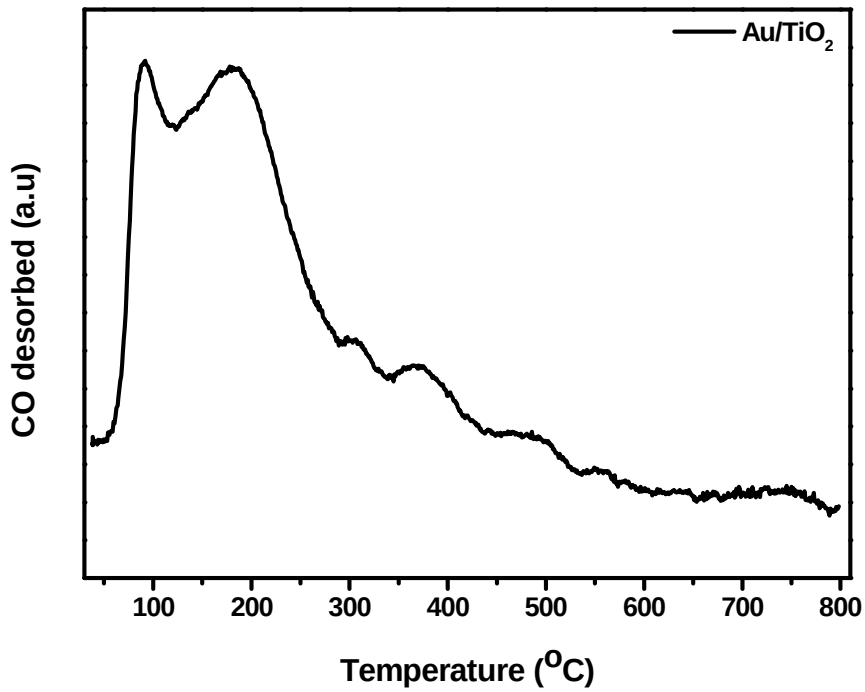


Figure 4.2: CO-TPD profile of Au/TiO_2 catalyst

Figure 4.2 illustrate two prominent peaks of CO_2 desorbed at 100 and 200°C. The area under the peaks is indicative of the amount of CO adsorbed on the active sites and also indicates the abundance of active sites. The studies conducted by Triphathi et.al. showed high activity of Au/Fe_2O_3 which was attributed to CO chemisorbed on small Au particles [25]. The low coordinated Au atoms are important for high catalytic activity of Au catalysts [23]. It has also been reported in the literature that the relative concentration of these low coordinated Au atoms responsible for catalytic activity is size dependent [23]. Hence low coordinated small sized Au particles are important for achieving high catalytic activity. It can be assumed that more CO_2 desorption observed at low temperatures is due to the high availability of low coordinated Au atoms on the surface, particularly small sized Au particles. According to studies conducted by Nørskov's group strongly indicated that CO may only chemisorb on the low-coordinated Au atoms such as steps and kinks, and not on the regular (111) terraces [26]. Therefore it is not known which active sites are responsible as CO chermisorption studies were not performed.

There are desorption peaks observed at temperatures above 300 °C that are not so pronounced, peaks at 305, 375 and 480 °C. The adsorption of CO on the active site decreases with increasing temperature, hence we observe a decrease in peak area at temperatures above 300 ^{o}C. This suggests that as temperature increases the low coordinated Au atoms on the

surface decreases. Hereby suggesting that there could be particle sintering occurring at high temperatures since small gold particles are necessary to provide CO adsorption sites [26]. Other authors reported that very large particles have much smaller relative concentration of step-edge sites thus providing low activity [26]. Boccuzzi et al. observed the rate of CO oxidation reaction increasing with decreasing diameter of Au particles [27].

The particles size of the Au/TiO_2 catalysts after CO oxidation was monitored by TEM (Fig 4.3). Figure 4.3a illustrates the particle size before catalytic measurements were carried out. It is observed that particle size is 3.7 nm prior catalytic evaluations. There is a slight decrease in particle size for the catalyst at 300 °C. The measured particle for catalyst at 300 °C is 3.5 nm. Therefore a decrease in activity observed for 300 °C (Fig 4.1) could be due to surface reconstruction decreasing the available surface sites. It was also observed that the particle size of the catalysts at 400 and 500 °C was 4.5 nm. This could explain the conversion observed for both catalysts at 400 and 500 °C. The catalyst at 600 °C was found to have a particle size of 4.25 nm, a decrease compared to catalysts at 400 and 500 °C. The particle size effect may explain the slight difference in activity. A decrease in CO conversion could be attributed to the increasing particle size which results from large particle aggregates. A plot of conversion vs particles size (Fig 4.4) at 300 min shows that as mean particle size increases CO conversion decreases. However, the 4.5 nm particles shows high conversion than 4.25 nm suggesting that there are other factors influencing the activity of the catalyst. Since $HAuCl_4$ was utilized as source of Au during synthesis it can be assumed that chlorine contaminants could be responsible for declining activity of the Au/TiO_2 catalyst.

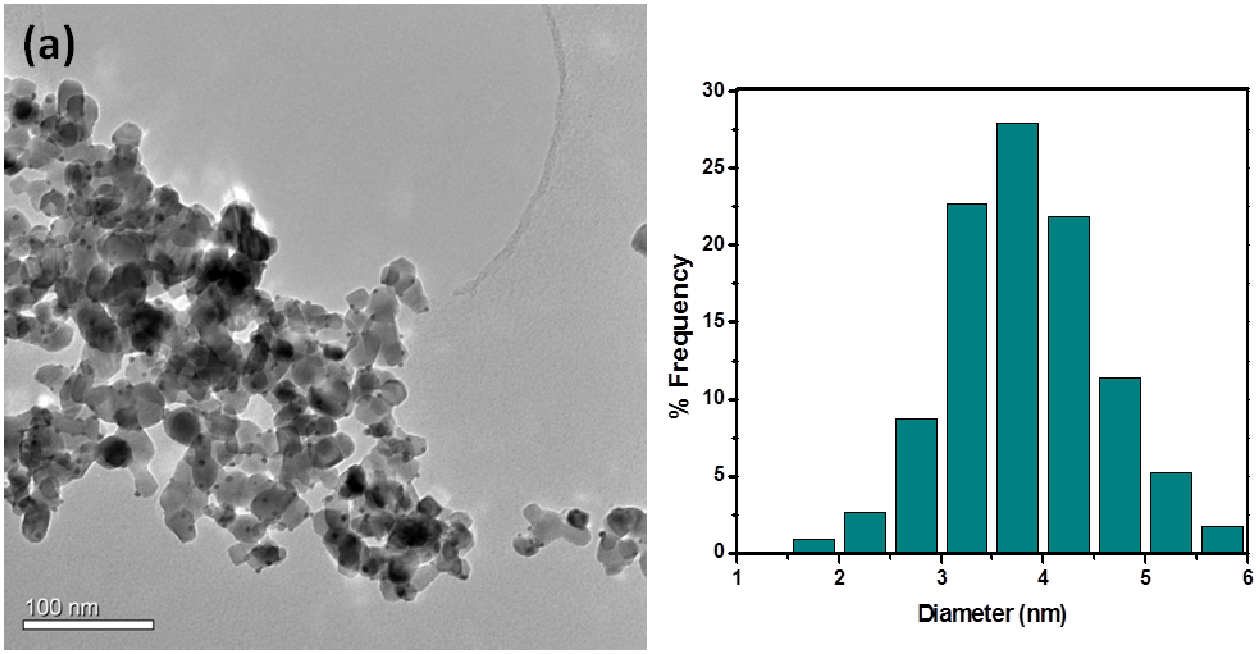


Figure 4.3a: TEM image and particle size distribution of Au/TiO_2 catalyst prior catalytic evaluation.

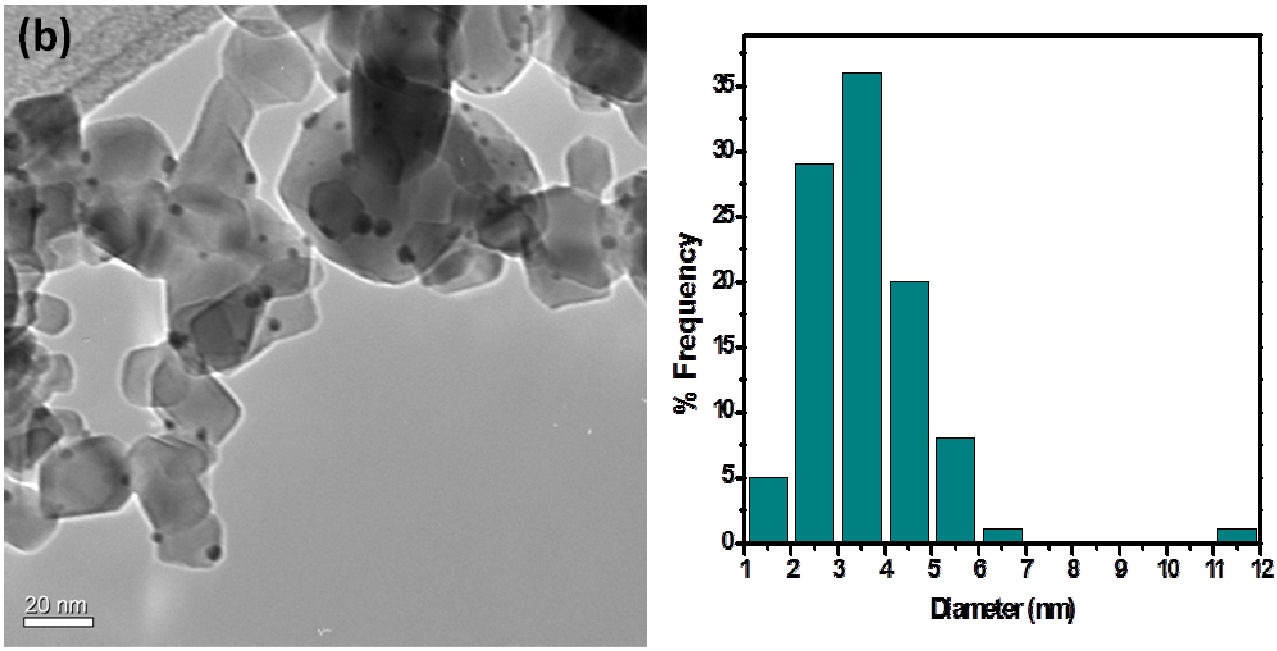


Figure 4.3b: TEM image and particle size distribution of Au/TiO_2 catalyst after catalytic evaluation at temperature 300 °C.

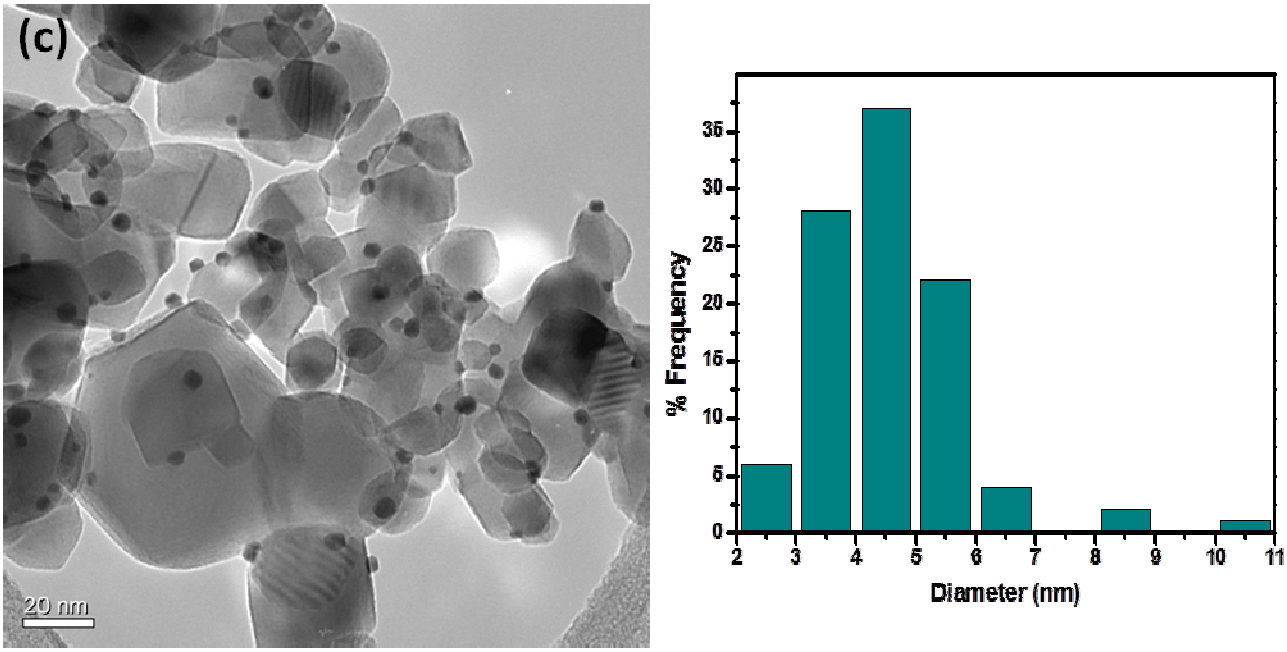


Figure 4.3c: TEM image and particle size distribution of Au/TiO_2 catalyst after catalytic evaluation at temperature 400 °C.

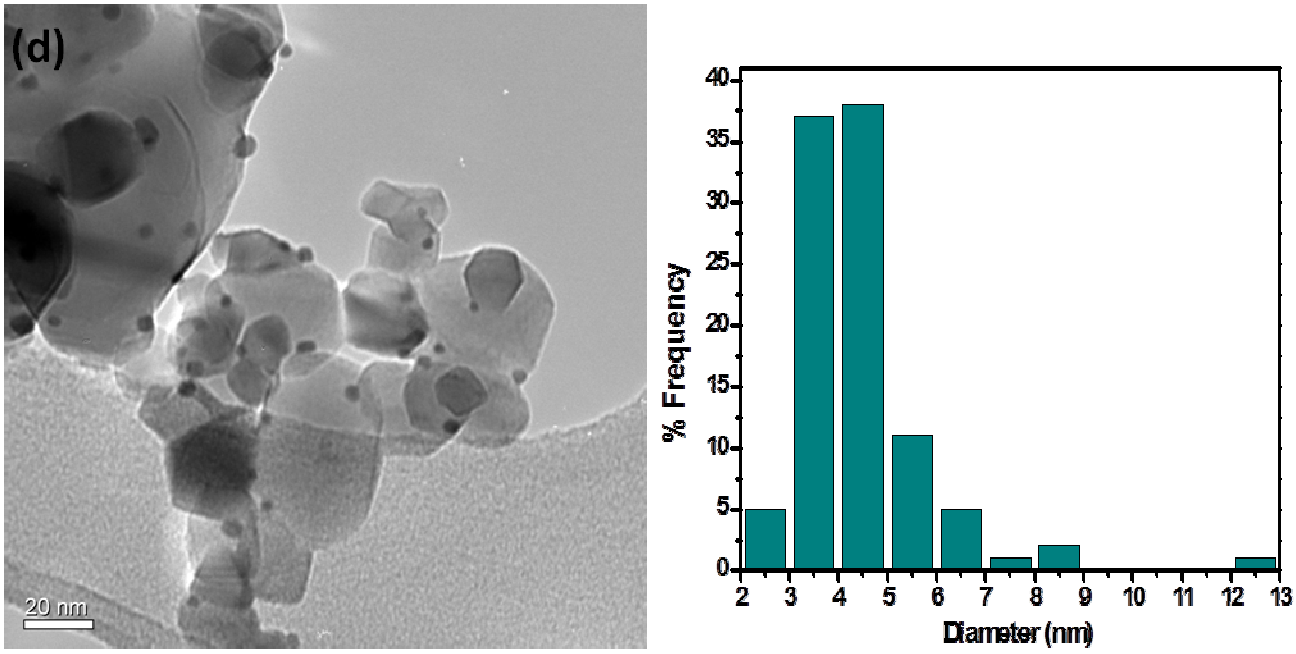


Figure 4.3d: TEM image and particle size distribution of Au/TiO_2 catalyst after catalytic evaluation at temperature 500 °C.

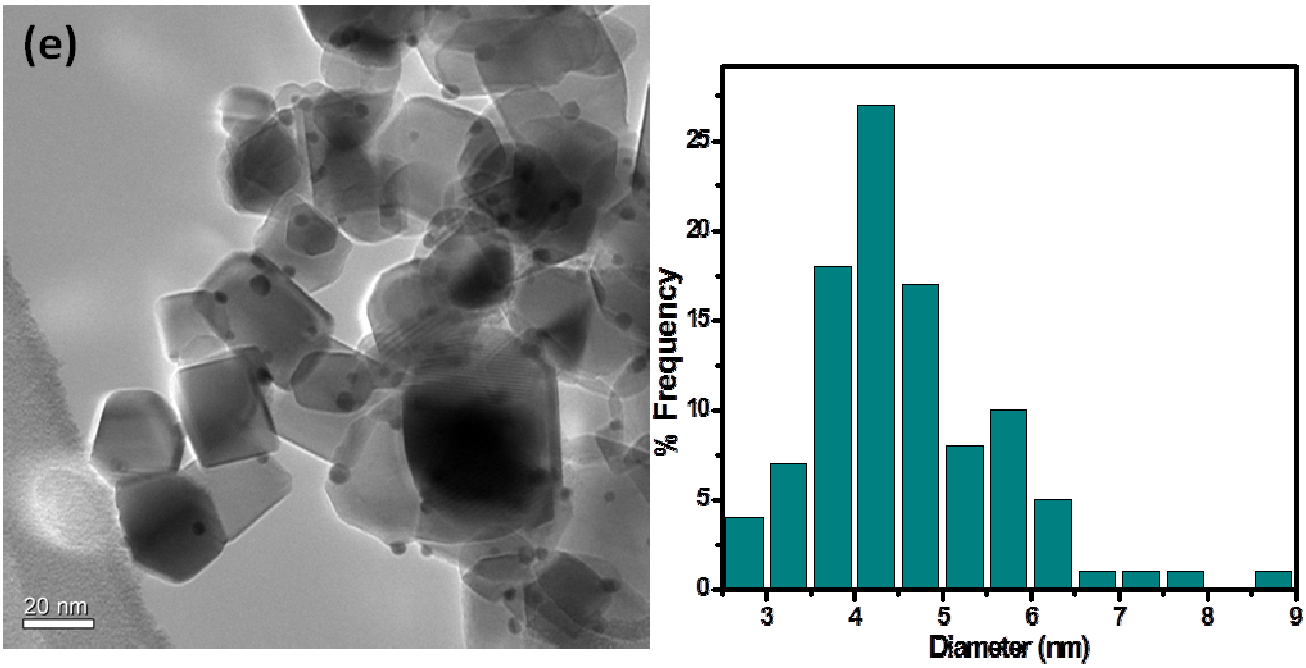


Figure 4.3e: TEM image and particle size distribution of Au/TiO_2 catalyst after catalytic evaluation at temperature 600 °C.

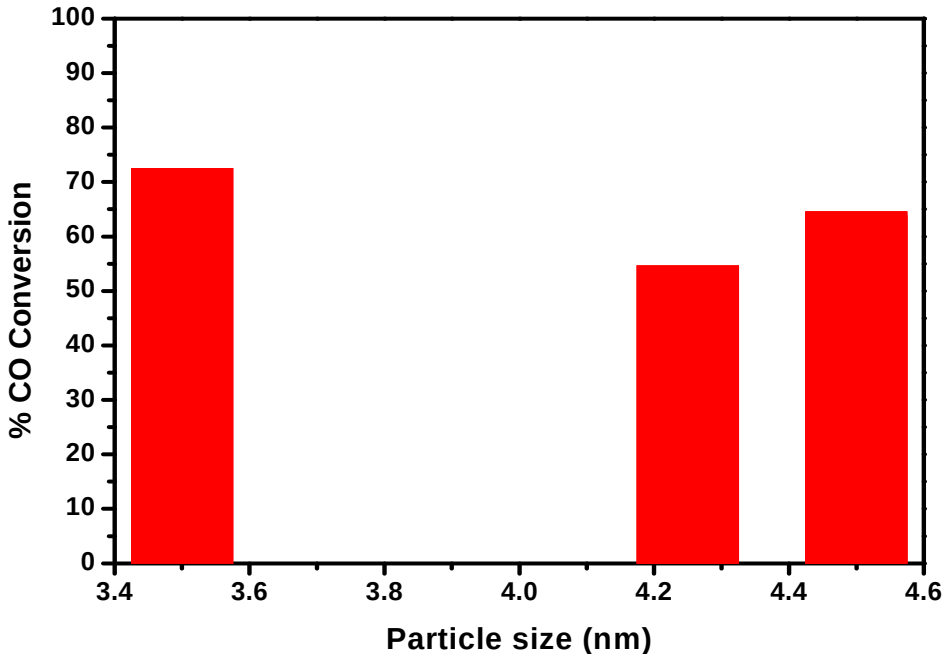


Figure 4.4: Graph of % CO Conversion vs particles size at 300 min.

4.3.2 CO oxidation over Au-Pd/TiO_2

The supported Au-Pd metal have catalysts have been used in some important reactions such as hydrogenation of acetylene, aromatics, direct oxidation of hydrogen peroxide, oxidation of carbon monoxide [30-29]. The use of second metal is known to introduce new geometry and electronic properties of the active sites [28]. However, the catalytic performance is dependent on factors such as catalyst support, preparation procedure, composition and morphology. Guczi et al. revealed the synergistic effect in Au-Pd nanoparticles supported on TiO_2 compared to monometallic samples [29]. Yang et al. found that unsupported bimetallic Au-Pd, Cu-Pd, and Cu-Pd exhibited excellent activity for CO oxidation, indicating the influence of the support on the catalytic activity for the reaction. In this investigation Pd metal has been used as a typical promoter for enhancing catalytic activity of Au/ TiO_2 catalyst. The choice of Pd metal is dictated by its well recognized activity in this type of reaction [31].

From the preliminary results in Chapter 3 it was found that the bimetallic system formed after incorporating Pd was heterostructured bimetallic systems were both Pd and Au metals were separately attached on the surface of the support. There was no PdO or Au-Pd detected thus suggests that palladium was in its reduced form.

This section investigate the effect of palladium on CO oxidation over Au/TiO_2. Catalysts with different palladium to gold ratios were prepared by deposition precipitation at pH =8 and catalytic oxidation of CO was performed at 200 ^{o}C.

4.3.2.1 CO oxidation over Au-Pd/TiO_2 with various Au and Pd loading

A CO conversion above 90% was obtained with the monometallic Au catalyst at 200 °C shown in Fig 4.1. To investigate the effect of Pd metal on the Au catalysts, all the CO oxidation measurements were carried at temperature 200 °C. The observed conversion of bimetallic catalysts (Fig 4.5) is low compared to the monometallic catalyst (Fig 4.1) regardless of the various metal ratios This is in total agreement with the findings of Piednoir et al. who demonstrated the presence of palladium in bimetallic Au catalysts decreases the CO oxidation activity [32]. Furthermore, addition of Au decreased the activity of Pd, where high activity was observed for Pd (111) compared to Pd-Au [32].

There is low conversion observed for the first hour for all catalysts except for catalyst with 75Au25Pd composition where there is no conversion for at least the first 2 h on stream. The 0% conversion observed for 75Au25Pd in the first hour could be due to no CO adsorption occurring as CO desorption on Pd sites is a rate limiting step [33]. 75Au25Pd seems to be the only catalyst not showing decline in conversion with increasing time on stream. However, the inconsistency observed for 75Au25Pd catalyst requires that the CO oxidation measurements are repeated to verify the results. The increasing trend is similar for monometallic catalysts (Fig 4.1). It is also seen that for the catalyst with 90Au10Pd metal composition showed high activity for the first 5 h on stream, which is followed by a decrease in conversion reaching a minimum of 58%. The catalyst with equal metal composition showed 95% conversion after 2h on stream which declines to 65% conversion. The lowest conversions were observed at 8 h for both 50Au50Pd and 25Au75Pd which followed by a rapid increase in CO conversion. This increase suggests that there could be phase changes taking place. Liu et al. demonstrated a detailed transition process during heating all types and sizes of Au clusters [36]. He found that there was structure transition that occurred by changing orientation [36].

There was a decrease in conversion observed for 90Au10Pd catalyst after 10 h, at which there was an increase in conversion observed for both 50Au50Pd and 25Au75Pd. The decrease in conversion could be due to high content of Pd which inhibits the dissociation oxygen on the gold particles [35]. At high palladium concentrations, palladium seems to be blocking gold active sites from adsorbing oxygen molecules. The decrease in CO conversion with increase in time on stream can be attributed to the decrease in stability. This behavior is only observed with the palladium containing catalysts. These results suggest that the presence of palladium is not helping in improving the activity of the gold catalyst. However, there is a measure of consistency in that all the Pd-containing catalysts show an induction period.

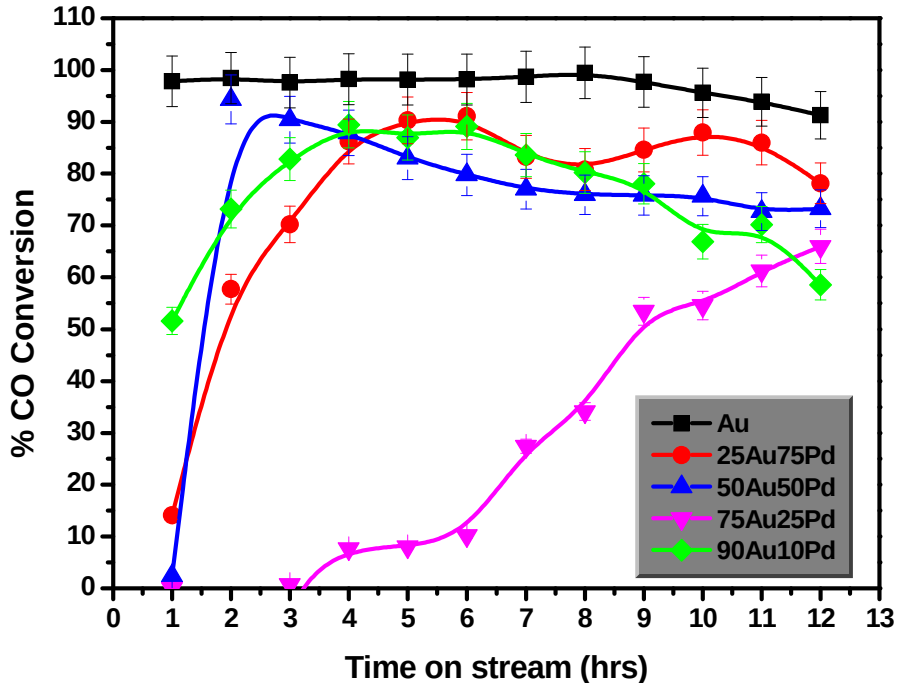


Figure 4.5: CO oxidation activity as a function of time on stream on Au-Pd/TiO_2 of various Au and Pd metal loadings at temperature 200 °C.

Fig 4.6 contains CO-TPD profiles of Au-Pd/TiO_2 catalysts with different metal ratios. At low temperatures there is high CO desorption which increases with increasing Pd content. A decrease in CO desorption was observed with increasing temperature. This suggests that there is less number of active sites at high temperatures. There is an intense peak observed for bimetallic catalysts at approximately 560 °C which is not observed for Au/TiO_2 catalyst. This could suggest that at high temperatures CO adsorb on Pd active sites. There is a similar trend observed for both 25Au75Pd and 75Au25Pd were there are no peaks observed at approximately 360 ° and 470 °C suggesting that the Au active sites are only available at low temperatures and the Pd active sites are only present at high temperatures. According to literature CO oxidation is able to take place at low temperatures on the Au-Pd surface due to the alloying effect [27]. This is due to the weak CO-Pd interaction which favours the adsorption of O_2 and promotes oxidation of CO [27]. Therefore the Pd active sites at low temperatures are only available on Pd-Au alloys. TEM (Fig 4.7) shows small particle size of 2.7 nm for 25Au75Pd catalyst and 4.5 nm particle size for 75Au25Pd catalyst. This indicates that as Pd loading increases, particles size decreases. The superior activity observed for 25Au75Pd catalyst can be attributed to a decreased particle size. However, it is observed that for catalyst with 90Au10Pd the peak at 360 °C is more intense than the peak at 470 °C and vice versa for the 50Au50Pd catalyst. The intense peak observed at 470 °C for 50Au50Pd

catalyst suggests that Pd metal could be the responsible for CO adsorption at high temperatures.

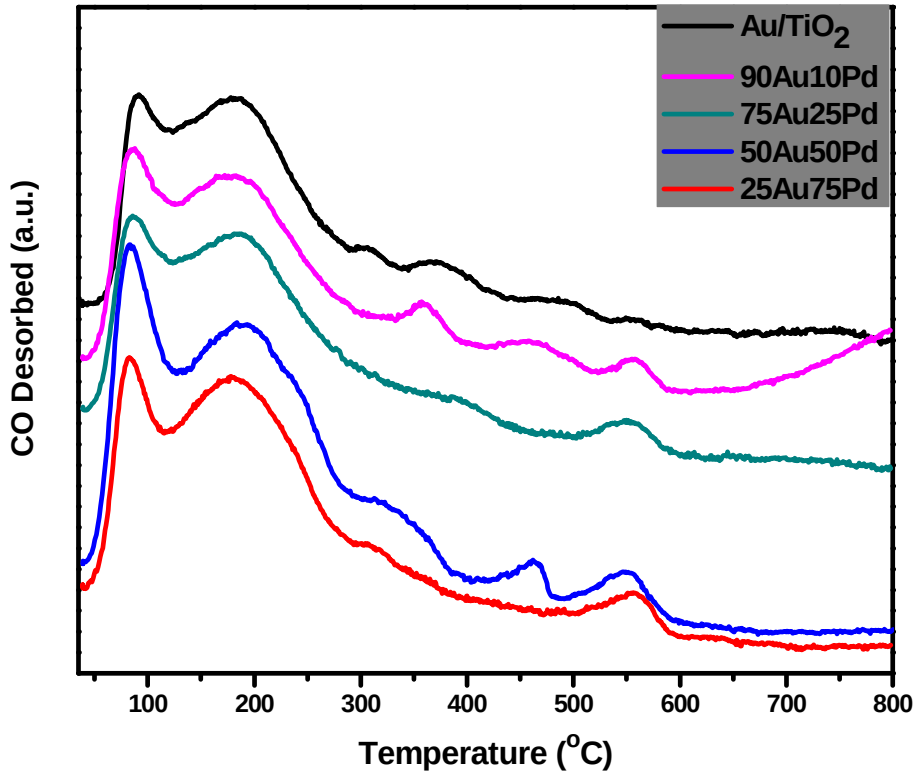


Figure 4.6: CO-TPD profiles of Au/TiO_2 and $Au-Pd/TiO_2$ catalysts.

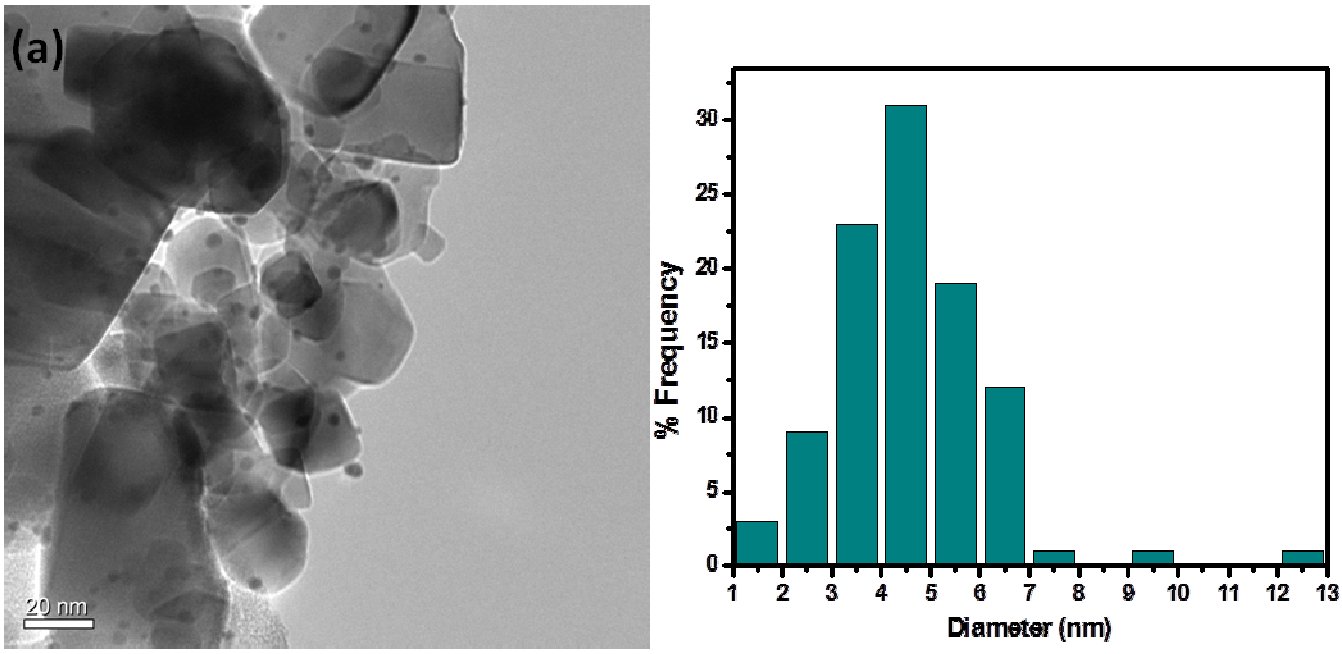


Figure 4.7a: TEM image and particle size distribution of 75Au25Pd catalyst after catalytic evaluation at temperature 200 °C.

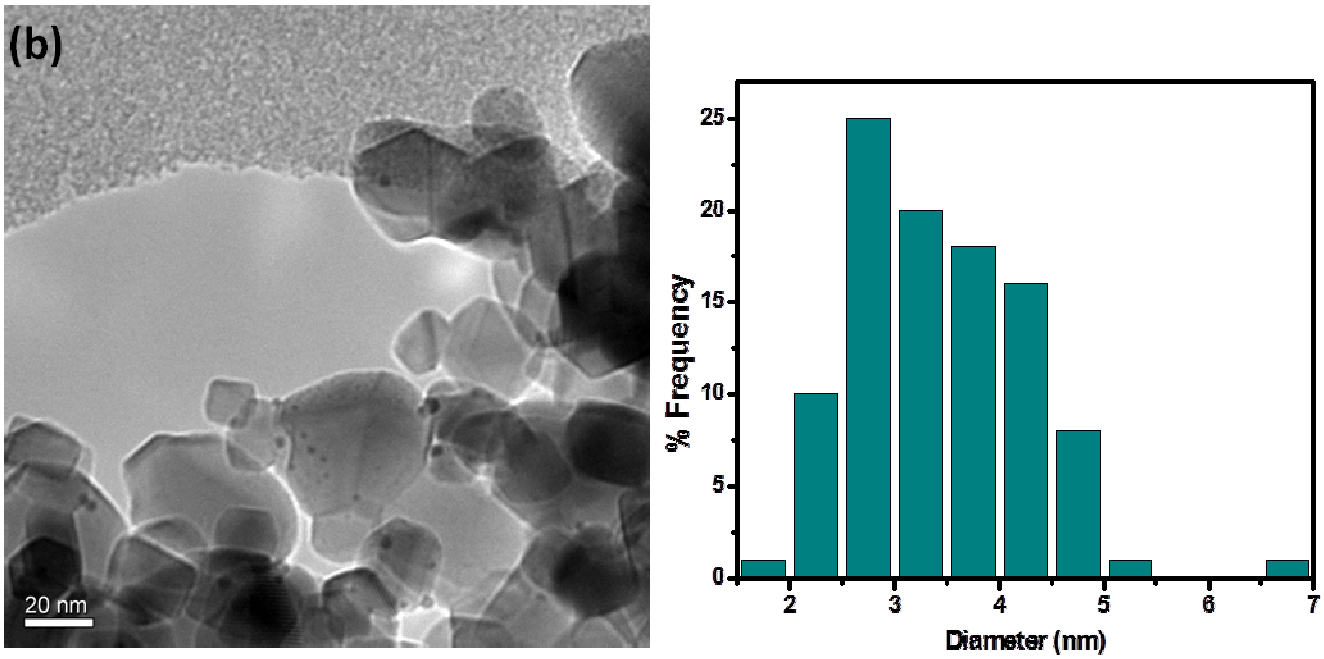


Figure 4.7b: TEM image and particle size distribution of 25Au75Pd catalyst after catalytic evaluation at temperature 200 °C.

4.3.2.2 Temperature studies of 25Au75Pd catalyst

Temperature studies (Fig 4.8) were performed with a catalyst that showed high activity at 200°C which is 25Au75Pd. The CO oxidation measurements were carried at temperatures 200, 300 and 400 °C. It is observed that as the temperature increases conversion decreases. However, there is an increase in activity observed at from 8 to 10 h for both 200 and 300°C. Further increase is observed for 300 °C with 95% CO conversion. The observed increase suggest that there be could catalysts restructuring taking place which introduces new active sites. Liu et al. reported that morphologies of Au clusters changes with increasing temperatures [36].

The TEM studies conducted by Prati et al. on Au-Pd/C catalyst after selective liquid phase oxidation of glycerol to glycerate indicated that the metal particles were assembled after the reaction [35]. Moreover, the activity of the catalysts was not compromised. The presence of Au-Pd phase resulted in increased activity thus introducing strong synergetic effects [35]. On the other hand catalyst at 400 °C shows a steady decrease in activity. This could be ascribed to a decrease in active sites resulting from particle growth. It is also observed that the catalyst stability declines with an increasing time on stream except for 300 °C which shows high CO conversion. The inconsistencies observed in these results could be due to the absence of PdO and alloyed Au-Pd phase which are known to accelerate activity of Au-Pd/TiO_2 catalysts. The observed results suggest that the optimum operating temperature of the 25Au75Pd catalyst could be between 200 and 400 °C. Furthermore, decreased activity observed could be attributed to the preparation method used as there was no surfactant used to control morphology and composition of the catalyst. Again, there was no surface analysis performed during and after catalytic measurements to monitor whether there is surface restructuring taking place.

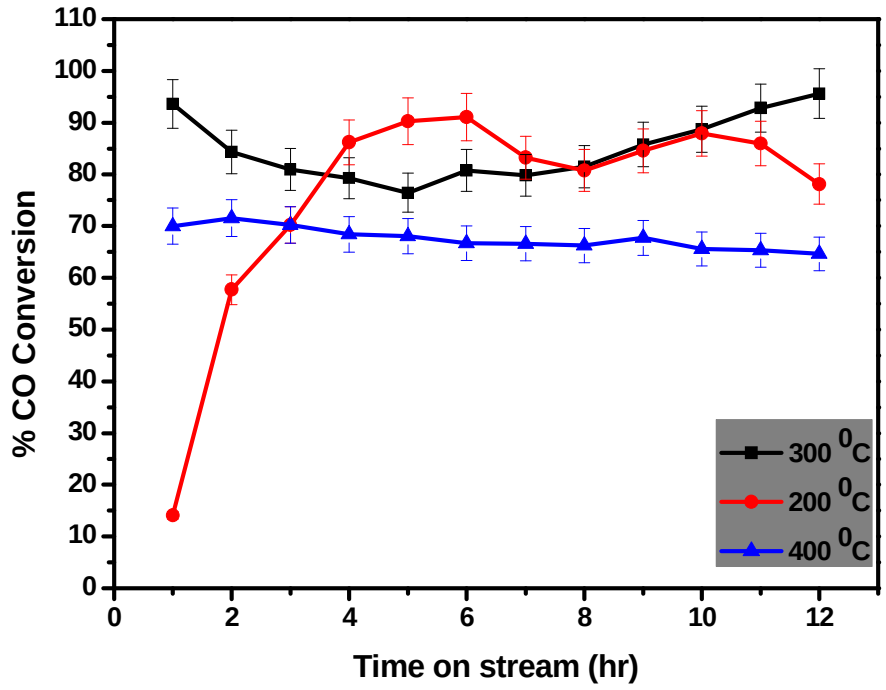


Figure 4.8: CO oxidation activity as a function of time on stream on 25Au-75Pd/TiO_2 at various temperatures

4.4 Conclusion

A simultaneous deposition of Au and Pd metals via DP method resulted in formation of separately attached metals on the support instead of AuPd alloy or core shell. Therefore DP method proved to be not an appropriate method for synthesizing Au-Pd bimetallic. Based on the findings presented above it can be concluded that incorporating Pd metal resulted in decreased particle size of Au metal. However, the monometallic catalysts showed high activity compared to bimetallic catalysts. High CO conversion for monometallic catalysts is observed at 200 °C. TPD results confirmed that at low temperatures there are more CO adsorption sites for both monometallic and bimetallic catalysts. However, the CO adsorption sites increases with increasing Pd particularly at high temperatures. Hence the peak at approximately 550 °C becomes more intense as Pd loading increases. The catalysts stability of both monometallic and bimetallic declines with increasing time on stream which could be due to the decreasing amount of active sites. The cause of deactivation of Au-Pd catalyst was not studied further studies are recommended.

4.5 References

[1] J. A. Moma, PhD Thesis, University of the Witwatersrand, Johannesburg, **2007**

[2] M. Götz, H. Wendt, *Eletrochimica Acta*, 43 (**1998**) 3637

[3] B. Rohland, V. Plzak, *J. Power Sources*, 84 (**1999**) 183

[4] A. Luengnaruemitchai, S. Osuwan, E. Gulari, *Int. J .Hyd. Energy*, 29 (**2004**) 429

[5] D. M. Nicholas, Y. T. Shah, *Ind. Eng. Chem*, 15 (**1976**) 1

[6]http://www.platinum.matthey.com/uploaded_files/int_2008/09special_featurepdindieselcatalysts.pdf, 06 March **2012**

[7] M. Haruta, S. Tsubota, T. Kobayashi, H. Kayeyama, M. J. Genet, B. Delmon, *J. Catal*, 114 (**1993**) 175

[8] D. Cameron, R. Holliday, D. T. Thompson, *J. Power. Sources*, 118 (**2003**) 298

[9] L. Guczi, *Catal. Today*, 53 (**2005**) 101

[10] A. E. Hahelin-Weaver, J. F. Weaver, G. B. Hoflund, G. N. Salaita, *J. Alloys Comp*, 393 (**2005**) 93

[11] Y. Robach, M. Abel, L. Porte, *Surf. Sci*, 526 (**2003**) 248

[12] M. Chen, D. Kumar, C. W. Yi, D. W. Goodman, *Science*, 310 (**2005**) 291

[13] M. Haruta, *Catal. Today*, 36 (**1997**) 153

[14] N. M. Gupta, A. K. Tripathi, *Gold Bulletin*, 34 (**2001**) 120

[15] J. Turkevich, *Gold Bulletin*, 18 (**1985**) 86

[16] T. A. Ntho, PhD Thesis, University of the Witwatersrand, Johannesburg. (**2008**)

[17] C. K. Castello, M.C. Kung, H. S. Oh, Y. Wang, H. H. Kung, *Appl. Catal. A*, 232 (**2002**) 159

[18] C. H. Kim, L. T. Thompson, *J. Catal*, 229 (**2005**) 600

[19] M. Daté, Y. Ichihashi, T. Yamashita, A. Chiorino, F. Boccuzzi, M. Haruta, *Catal.Today*, 72 (**2002**) 89

[20] S. Tsubota, Report of the Osaka National Research Institute No 393: Report of the Reseach Achievements of Interdisciplinary Basic Research Section (April 1994-March 1999) pp 36

[21] G. Y. Cha, G. Parravano, *J. Catal*, 18 (**1970**) 200

[22] R. Zanella, S. Giorgio, C.-H. Shin, C.R. Henry, C. Louis, *J. Catal*, 222 (**2004**) 357

[23] N. Lopez, T. V. W. Janssens, B. S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, J. K. Nørskov, *J. Catal*, 223 (**200**4) 232

[24] G. C. Bond, D. T. Thompson, *Gold Bulletin*, 33 (**2000**) 41

[25] A. K. Tripathi, V. S. Kamble, N. M. Gupta, *J. Catal*, 187 (**1999**) 332

[26] M. Mavrikakis, P. Stoltze, J. Nørskov, *Catal. Lett*, 64 (**2000**) 10

[27] F. Boccuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa, M. Haruta, *J Catal*, 202 (**2001**) 256

[28] A. M Venezia, L. F, Liotta, G. Pantaleo, V. La Parola, G. Deganello, A. Beck, Zs. Koppány, K. Frey, D. Horváth, L. Guczi, *Appl. Catal A*, 251 (**2003**) 359

[29] J. K. Edwards, B. Solsona, P. Landon, A. F. Carley, A. Herzing, M. Watanabe, C. J. Kiely, G. J. Hutchings, *J. Mater. Chem*, 15 (**2005**) 4595

[30] M. A. Centeno, I. Carrizosa, J. A. Odriozola, *Appl. Catal. A:Gen*, 246 (**2003**) 365

[31] A. Piednoir, M. A Languille, L. Piccolo, A. Valcarcel, F. J. Aires, J.C. Bertolini, *Catal Lett*, 114 (**2007**) 1

[32] P. London, P. J, Collier, A. J. Papworth, C. J. Kiely, G. J. Hutchings, *Chem Commun*, (**2002**) 2058

[33] S. Fuchs, T. Hahn, H. G. Lintz, *Chem Eng. Processing*, 33 (**1994**) 363

[34] K. Frey, V. Iablokov, G. Melaet, L. Guczi, N. Kruse, *Catal Lett.*, 124 (**2008**) 74

[35] L. Prati, M. Rossi, *J. Cata.*, 176 (**1998**) 552

[36] H. B. Liu, J. A. Ascencio, M. Perez-Alvarez, M. J. Yacaman, *Surf. Sci*, 491 (**2001**) 88