Pakistan Academy of Sciences

Research Article

Effect of Support on Catalytic Efficiency of Au-Pd Bimetallic Catalysts

Noreen Sajjad[1, 2], Ayesha Sultan[3*], Syeda Laila Rubab[3], Fozia Batool[1],
Muhamamd Zuber[2], Shagufta Saeed[4], Ghulam Hussain[1], and Roberto Acevedo[5]

[1]Department of Chemistry, University of Sargodha, Sargodha-40100, Pakistan
[2]Department of Chemistry, University of Lahore, Lahore-54000, Pakistan
[3]Department of Chemistry, Division of Science & Technology,
University of Education, Lahore-54000, Pakistan
[4]Institute of Biochemistry & Biotechnology, University of Veterinary & Animal
Sciences, Lahore-54000, Pakistan
[5]Facultad de Ingenieria y Tecnologia, Universidad San, Sebastian Bellavista 7,
8420524 Santiago, Chile

Abstract: The supported Au-Pd based bimetallic catalysts nanomaterials have attracted mounting research attention for applications in diverse fields of pharmaceutical, fragrance industry and nanotechnology. In the present study, we have undertaken a detailed investigation on synthesis and catalytic activity studies for selective oxidation of benzyl alcohol by various Au-Pd supported catalysts on different supports & with different metal ratios. The support systems were prepared by simple physical grinding protocol. The catalytic performance of supported bimetallic catalysts was evaluated on the basis of selectivity and TOF. The results of this study confirm that efficiency of catalysts is highly dependent on the nature of the support and also dependent on metal ratios.

Keywords: Oxidation, Heterogeneous catalysis, Au-Pd bimetallic catalysts, Benzyl alcohol, Supports, Benzaldehyde.

1. INTRODUCTION

With diminishing natural resources and increase in pollution, green chemistry is gaining grounds in current era and attempts are being made to develop cost effect and environmental friendly processes for the production of fine and commodity chemicals. Tailoring/ designing of new catalysts that can provide selective and high product yield is the need of time. Recently, a number of research groups have taken special interest in gold and palladium based bimetallic heterogeneous catalysts for activating small molecules such as CO, O_2, H_2, etc for cost effective chemical transformations [1]. The choice of support is of prime importance in the heterogeneous catalysis. The rationale of using support is to stabilize catalytic nanoparticles, optimize activity and decrease the amount of costly metal being utilized. Moreover, the supports promote dispersion of catalyst nanoparticles and improve catalytic activity by assisting in electron transfer phenomenon.

Since the support may sometime exert a structural effect on catalyst, brought about by textural and active phase-linked effect a suitable support will be the one on which the heterogeneous catalyst retains its specific properties, such as porosity, surface area, dispersion, selectivity, and activity. The catalytic performance of Au heterogeneous catalyst is mainly determined by particle size and properties of the support [2-3]. In general, it has been observed that when reducible metals are coupled with gold, the catalytic activity has been found to increase up to an order of magnitude than same gold on irreducible support.

The reducible supports have advantage of being tolerant to increased gold particle size while still maintaining reasonable activity.

For a supported catalyst to be effective for a given transformation, it is necessary to have strong interactions between metal and support, tunable porous surface & distribution, high thermal stability, mechanical strength and acid-base properties [4]. Same catalyst dispersed over different support yield different results for a given transformation. As for example, Edward et al., showed that metals supported over activated carbon (G60) are more effective catalysts for the direct synthesis of H_2O_2 as compared to other oxide supports [5]. While ceria supported catalysts [6] and Au-Pd catalysts supported over Gallia have been reported to be effective for the oxidation of alcohols [7].

Benzyl alcohol is a common model substrate for studies of selective oxidation of primary alcohols. In our previous work we studied the varying Au-Pd (weight) ratio with total 5% metal loading over titania, [8]. The present work is concerned with preparation and use of different supports with Au-Pd bimetallic catalysts for solvent free selective oxidation of benzyl alcohol to benzaldehyde as shown in scheme 1.

2. MATERIALS AND METHODS

All the chemicals used in this study were of analytical grade and we used them without further purification. In all experiments, double distilled water was used. All qualitative & quantitative analysis was performed on Gas Chromatography (Varian 3800, CP-wax column).

2.1 Preparation of catalysts

A range of Au-Pd bimetallic catalysts with 5% total metal loading with equal Au and Pd metal ratio of 1:1 ratio were prepared by physical mixing followed by grinding of different supports [namely TiO_2 (Degussa P25, Sigma Aldrich), Carbon (Darco G60, Sigma Aldrich), ZrO_2 (Sigma Aldrich), CeO_2, nanopowder (Degussa AG. Sigma Aldrich) and MgO, Sigma] with gold (III) acetate (Alfa Aesar 99.9%) and palladium (II) acetate (Sigma Aldrich 99.9%) in a mortar and pestle for 10-15 minutes. The resultant mixture was placed in a 4-inch ceramic boat and placed in tubular furnace at 350 °C for 2 h at ramp rate of 5 °C min-1 for heat treatment or calcination under the flow of He gas to facilitate the decomposition of the acetate precursors to form metal particles.

2.2 Benzyl Alcohol Oxidation

An autoclave was used for catalyst testing at 140 °C and maximum pressure of 10 bar. After loading the benzyl alcohol (40 mL) and catalyst (25 mg) into stainless steel autoclave vessel, autoclave was purged three times with oxygen at 10 bar. The experiments were performed at constant pressure of 10 bar, 1500 rpm stirring rate, constant temperature
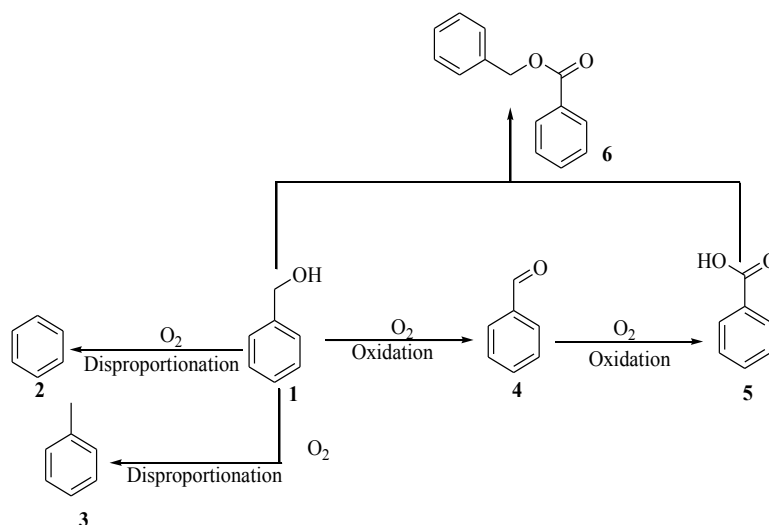
Scheme 1: Reaction pathways for benzyl alcohol oxidation; 1 Benzyl Alcohol, 2 Benzene, 3 Toluene, 4 Benzaldehyde, 5 Benzoic Acid, 6 Benzyl Benzoate [9]

of 140 °C and with continuous supply of oxygen. Samples were brought to the reactor after every 30 minutes through a sampling pipe.

3. RESULTS AND DISCUSSION

3.1 Effect of Support in the selective oxidation reaction

To track the effect of different supports on catalytic activity, a series of Au and Pd bimetallic catalysts were prepared on different supports namely: Carbon, TiO_2, CeO_2, MgO and ZrO_2. All the catalysts were prepared by physical grind method and calcined

at 350 °C for 2 h. Among all supports, carbon was found to be most active for the solvent-free oxidation of benzyl alcohol. Overall, all the oxide supports were found to be less effective than carbon. The reactivity of different support was found to be of the order: Carbon >TiO_2>CeO_2>ZrO_2>MgO.

Effect of supports on catalytic activity can be observed from the resultant time line profile in the above Fig. 1. Although Au-Pd supported on activated C (G-60) gave highest activity, however selectivity towards benzaldehyde is low due to formation of benzoic acid as a major product and the reaction had to be stopped after 1.5 hours due
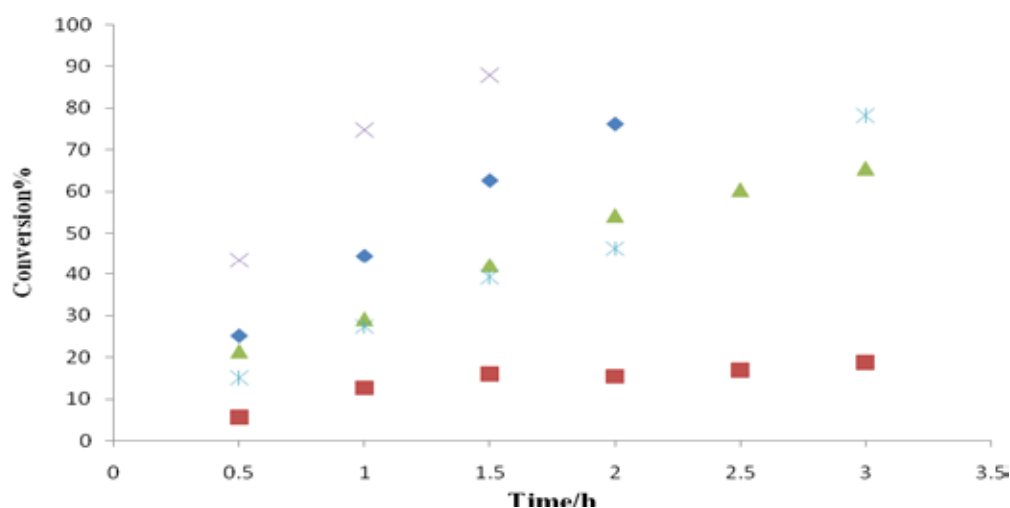

Fig. 1. The oxidation of benzyl alcohol over ♦2.5%Au+2.5%Pd/TiO_2, ■ 2.5%Au+2.5%Pd/MgO, ▲ 2.5%Au+2.5%Pd/CeO_2, × 2.5%Au+2.5%Pd/C and 2.5%Au+2.5%Pd/ZrO_2 at 140 °C with 10bar O2, Stirred at 1500rpm
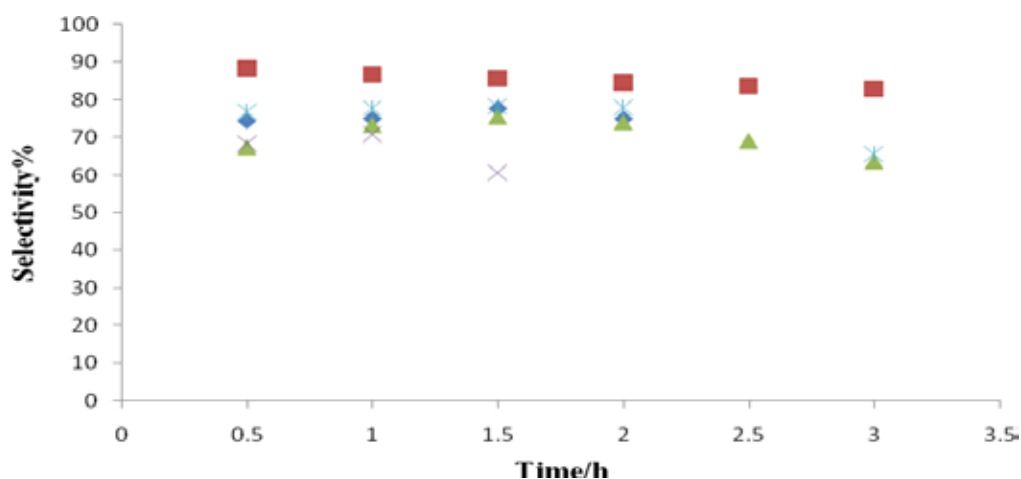

Fig. 2. The selectivity of benzaldehyde over ♦2.5%Au-2.5%Pd/TiO_2, ■ 2.5%Au-2.5%Pd/MgO, ▲ 2.5%Au-2.5%Pd/ CeO_2, ×2.5%Au-2.5%Pd/C and 2.5%Au-2.5%Pd/ZrO_2 at 140 °C with 10bar O_2, stirred at 1500 rpm.
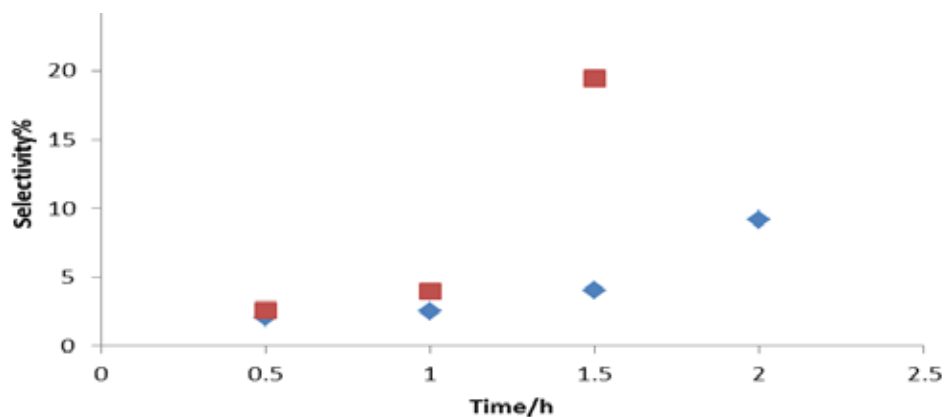
Fig. 3. The selectivity of benzoic acid over ♦2.5%Au-2.5%Pd/TiO$_2$, ■ 2.5%Au-2.5%Pd/C, at 140 °C with 10bar O$_2$, stirred at 1500 rpm
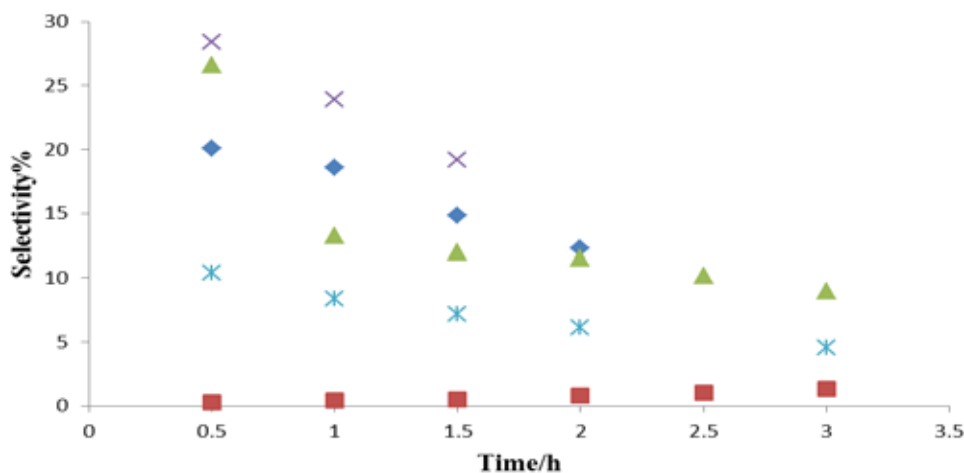

Fig. 4. Selectivity profile of toluene over ♦ 2.5%Au+2.5%Pd/TiO$_2$, ■ 2.5%Au+2.5%Pd/MgO, ▲ 2.5%Au+2.5%Pd/ CeO$_2$, ×2.5%Au+2.5%Pd/C and 2.5%Au+2.5%Pd/ZrO$_2$ at 140 °C with 10bar O$_2$, stirred at 1500 rpm.

to in situ oxidation of benzaldehyde (formed during reaction) to form which solidified in the reaction chamber as shown in Fig. 2 & 3.

Previous studies [4] have demonstrated that MgO supported catalysts can switch-off the disproportionation reaction for benzyl alcohol and hence promote the formation of benzaldehyde as a major product. In spite of high selectivity for benzaldehyde, the catalytic activity of the MgO support catalyst was the least amongst all supports as shown in Fig. 2 and formation of toluene is also very low because of complete switch-off of disproportionation reaction as compared to titania and other supports as shown in Fig. 3.

If we compare the results of TiO$_2$ and MgO supported catalysts the reason for this difference is mode of adsorption of benzyl alcohol at the

metal support interface for the disproportionation reaction. The difference in mode of adsorption can be attributed to the higher basicity of MgO support [4]. The Au-Pd catalyst supported over activated C exhibits higher selectivity towards toluene. The catalysts supported over ZrO$_2$ and CeO$_2$ also yields toluene as a major by-product however their selectivity towards toluene is lower than that observed for carbon supported catalysts. The MgO supported catalyst with 5% total metal loading shows lower activity as compared to its TiO$_2$ analogues. The 5%AuPd/TiO$_2$ catalyst resulted in approximately 88% conversion, whereas the 5%AuPd/MgO catalyst gave approximately 20% conversion.

In terms of effect of support on selectivity of benzaldehyde, the Au-Pd (MgO) shows the highest selectivity for benzaldehyde as compared to other

Table 1. The TOFs at 0.5h of the conversion of benzyl alcohol by catalysts prepared by the physical grinding method with total metal loading and 1:1 Au: Pd (weight) ratio on different supports.

| Catalysts	Support	TOF (h-1)
2.5%Au+2.5%Pd	TiO_2	42156
2.5%Au+2.5%Pd-	MgO	9311
2.5%Au+2.5%Pd	CeO_2	35983
2.5%Au+2.5%Pd	C	72756
2.5%Au+2.5%Pd	ZrO_2	25244

supports (as shown in Fig. 2). Because the use of MgO support switch off the disproportionation reaction. If we compare TiO_2 supported and MgO supported catalysts, there is a substantial increase in benzaldehyde selectivity of around 75% for the TiO_2 supported catalyst to 92% for the MgO supported catalyst. TiO_2 supported catalysts promote both oxidation and disproportionation reactions. Consequently, the overall higher activity for the TiO_2 supported catalyst is due to the additive contribution of both reactions, whereas the MgO supported catalyst only selectively promotes the oxidation reaction.

Detailed quantitative studies indicate that the interfacial sites between the nanoparticles and supports play a crucial role in the disproportionation reaction [4]. By changing the support from TiO_2 to MgO there is a complete switch-off in the disproportionation reaction, and thus toluene formation is very low in case of MgO support as compared to other supports. It is also observed that with the passage of time, there is a substantial decrease in toluene formation in case of all supports

except MgO. These results also show that oxidation promotes with time and disproportionation reaction is suppressed. The higher TOFs value for TiO_2 supported catalyst also supports the fact that the higher activity for TiO_2 supported catalyst is due to contribution of both oxidation and disproportionation reactions. While in case of MgO supported catalyst lower TOF value indicates that only oxidation is the dominant reaction (as shown in Table 1). The reason for this observed difference between the TiO_2 and MgO supported catalysts is speculated to be the mode of adsorption of the benzyl alcohol molecules at the metal–support interface for the disproportionation reaction. This difference in the mode of adsorption is attributed to the higher basicity of the MgO support [4, 10].

Table 1. The TOFs at 0.5h of the conversion of benzyl alcohol by catalysts prepared by the physical grinding method with total metal loading and 1:1 Au: Pd (weight) ratio on different supports.

Since the activity of C and TiO_2 supported catalysts is higher as compare to other supports , the
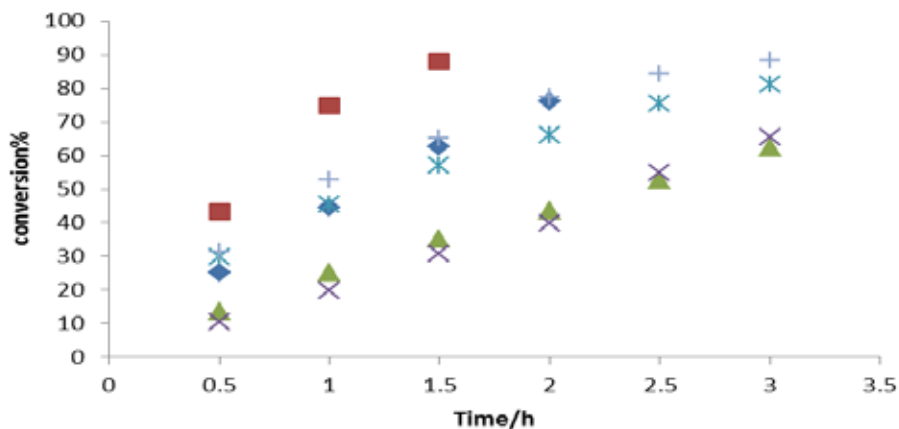
Fig.5. Oxidation profile of benzyl alcohol using ♦ 2.5%Pd+2.5%Au/TiO2, ■ 2.5%Pd+2.5%Au/C, ▲ 1%Pd-4%Au/TiO_2, × 1%Pd-4%Au/C, 4%Pd-1%Au/TiO_2, + 4%Pd-1%Au/C.

effect of Au-Pd ratio on the efficiency of supported catalyst for the solvent-free oxidation of benzyl alcohol was studied by employing various catalysts with total 5 wt% Au and Pd metals supported over TiO_2 and C with different Au and Pd ratios were prepared by physical grind method and tested for benzyl alcohol oxidation, as it is previously studied that TiO_2 is very efficient support for redox reactions [11-114]. The results obtained in the time-on-line data are shown in Fig. 5 with the corresponding selectivities towards benzaldehyde and toluene as shown in Fig. 6 and Fig. 7.

The catalyst with a 1:1 Au: Pd metal ratios showed the highest conversion for benzyl alcohol. The catalyst (1:4 Pd: Au) comprised largely of Au exhibit substantially lower conversion of benzyl alcohol than 1:1 Au-Pd catalyst for both supports C and TiO_2. Though, it is observed that the (4:1 Au: Pd) catalyst converts the twice as much as benzyl alcohol after 3 hours. So, a clear synergistic effect can be observed in the catalysts and ratios of metals also effect the conversion of benzyl alcohol. Because the molar mass of gold is approximately twice than palladium, So the catalysts having higher gold content have the less number of moles. Therefore, it is essential to standardize the initial activity of all catalysts with total 5% metal loading by turn over frequency (TOF= mol substrate converted per mol of metal per hour) as shown in Table 1 calculated at 0.5 h, which highlights the fact that a synergistic effect is present in gold and palladium bimetallic catalysts.

It has been observed that a monometallic Pd catalyst was significantly more active (TOF at 0.5 h of 34164 h[1]) than monometallic Au (TOF at 0.5 h of 18752 h[1]), no matter whether catalysts are prepared by physical grinding or other techniques. [15]. As, the mono metallic Pd catalyst shows highest conversion of benzyl alcohol but poor selectivity towards benzaldehyde higher activity to toluene, So the activity of monometallic Pd catalysts can be partially attributed to the disproportionation reaction [16]. The selectivity towards toluene is very similar for 1:4 Au-Pd catalysts supported over TiO_2 and C as shown in Fig. 7 and there is no significant difference in TOF values and the selectivity towards toluene is observed for 1:4 Au: Pd catalyst over TiO_2 and monometallic Pd catalyst

[16] But the selectivity of this 1:4 Au: Pd catalyst towards toluene suggests that monometallic palladium is dispersed active specie in this catalyst. The TOF value calculated for 1:4 Au: Pd catalyst at 0.5h is (30892 h[1]). But the selectivity of this 1:4 Au: Pd catalyst towards toluene suggests that monometallic palladium is dispersed active specie in this catalyst and vice versa for benzaldehyde selectivity.

The rational for this is that Au-Pd alloying cause a synergistic effect and 1:1 Au: Pd (TOF at 0.5 h of 42156 h[1]) catalyst shows highest conversion of benzyl alcohol and shows highest activity. This is due to clear synergistic effect and is indicative of alloy formation, which has been confirmed from STEM analysis performed on a PG 1:1 Au: Pd catalyst [15]. But, in terms of toluene selectivity had the lowest toluene selectivity of all Pd containing catalysts. Interestingly the lower activity of the gold rich 4:1 Au: Pd catalyst relative to the 1:1 Au: Pd catalyst was also accompanied by an increase in toluene selectivity, this is again implicit of minimal alloying, with the Pd be in a monometallic state suggesting that extensive alloying between gold and palladium will only occur if the metals are present in a certain ratio range [12, 14].

To provide a fair comparison of the selectivities to benzaldehyde and toluene Fig. 8 shows the selectivies at 60% iso-conversion for carbon and at 45% for TiO_2 support. These results of iso-conversion also support the results obtained from time on line data.

4. CONCLUSIONS

We have demonstrated that support effects the catalytic properties of the supported catalysts and can tuned the formation of products, such as by using MgO support disproportionation is switched off and thus the significant decrease in formation of toluene as a consequence a promising increase in the selectivity of aldehyde but at the cost of poor activity of catalyst as confirmed by TOFs values as compare to the other supports. This difference could be related to the surface composition or the redox conductance of the oxide supports and difference in mode of adsorption of substrate at metal support interface.
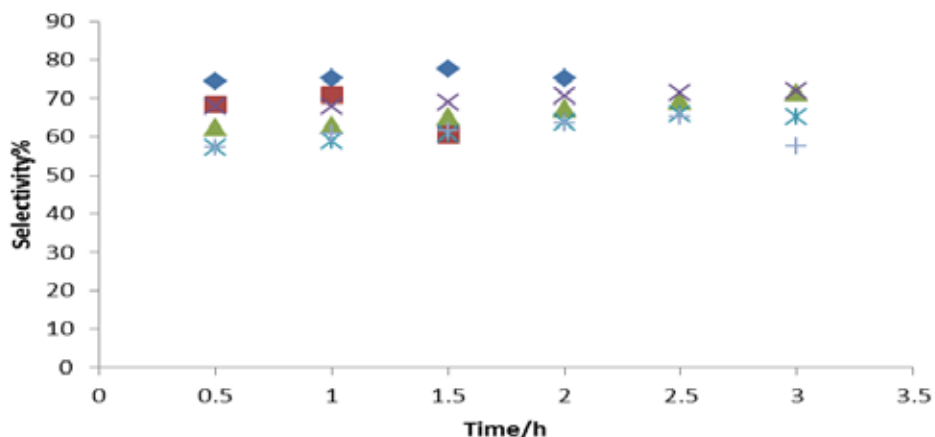
Fig. 6.   Selectivity profile of benzaldehyde using ♦ 2.5%Pd+2.5%Au/TiO$_2$, ■ 2.5%Pd+2.5%Au/C, ▲ 1%Pd+4%Au/TiO$_2$, ×1%Pd+4%Au/C, 4%Pd+1%Au/TiO$_2$, +4%Pd-1%Au/C
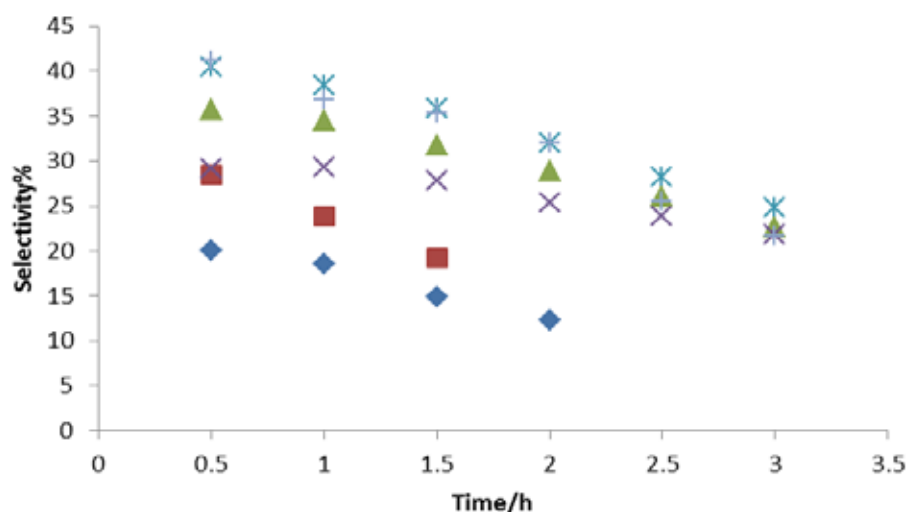

Fig. 7. Selectivity profile of toluene using ♦2.5%Pd+2.5%Au/TiO$_2$, ■2.5%Pd+2.5%Au/C, ▲1%Pd+4%Au/TiO$_2$,×1%Pd+4%Au/C, 4%Pd+1%Au/TiO$_2$, +4%Pd+1%Au/C
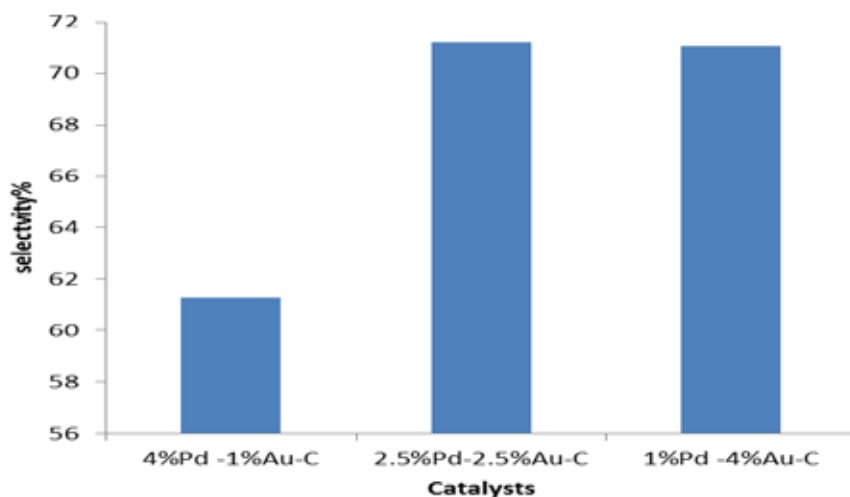

Fig. 8. Benzaldehyde selectivity profile of carbon-supported catalysts at 60% conversion
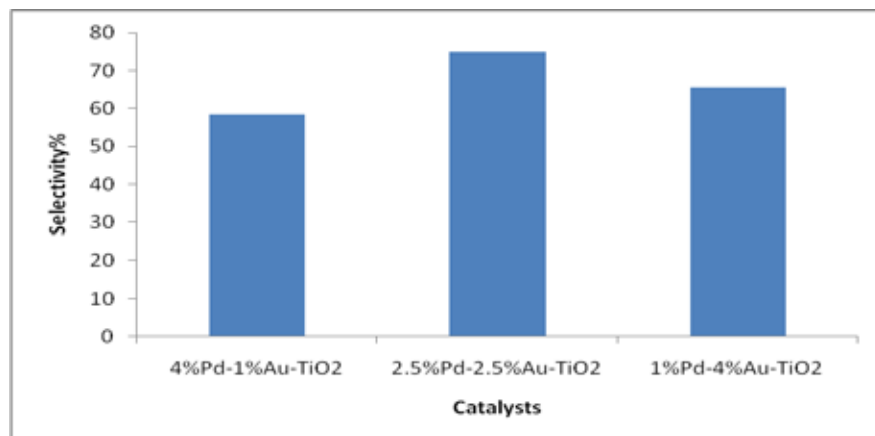
Fig. 9. Benzaldehyde selectivity profile of TiO_2-supported catalysts at 45% conversion

Table 2. Comparison of TOF for TiO_2 and C supported catalysts with different Au/Pd ratio

Catalysts		Support	TOF (h-1)
Pd (%)	Au (%)		
2.5	2.5	TiO2	42156
2.5	2.5	C	72756
1	4	TiO2	27958
1	4	C	21317
4	1	TiO2	30892
4	1	C	44700

5. ACKNOWLEDGMENTS

6. REFERENCES

1. Dimitratos. N., Lopez-Sanchez. J.A, & G.J. Hutchings. Selective liquid phase oxidation with supported metal nanoparticles, *Chemical Science.* 3: 20-44 (2012).
2. Li. B., P. He., G.Yi., H. Lin, & Y. Yuan. Performance of gold nanoparticles supported on carbon nanotubes for selective oxidation of cyclooctene with use of O2 and TBHP. *Catal Letters*. 133: 33–40 (2009).
3. Bawaked, S., N.F. Dummer., D. Bethell., D.W. Knight, & G.J Hutchings. Solvent-free selective epoxidation of cyclooctene using supported gold catalysts: an investigation of catalyst re-use. *Green Chemistry.* 13: 127-134 (2011).
4. Sankar, M., E. Nowicka., R. Tiruvalam., Q. He., H.S. Taylor., C.J. Kiely., D. Bethell., D.W. Knight, & G.J. Hutchings. Controlling the duality of the mechanism in liquid-phase oxidation of benzyl alcohol catalysed by supported Au-Pd nanoparticles *Chem. – European Journal.* 17: 6524-6532 (2011).
5. Edwards, J.K., A. Thomas., B.E. Solsona., P. Landon., A.F. Carley, & G.J. Hutchings. Comparison of supports for the direct synthesis of hydrogen peroxide from H2 and O2 using Au–Pd catalysts. *Catal. Today.* 122: 397-402 (2007).
6. Corma, A. & M.E. Domine, Gold supported on a mesoporous CeO2matrix as an efficient catalyst in the selective aerobic oxidation of aldehydes in the liquid phase, *Chem. Commun.* 4042-4044 (2005).
7. Su, F.-Z.; Liu, Y.-M.; Wang, L.-C.; Cao, Y.; He, H.-Y & K.-N Fan. Ga–Al Mixed-Oxide-Supported Gold Nanoparticles with Enhanced Activity for Aerobic Alcohol Oxidation. *Angew. Chem., Int. Ed.*, 47: 334-337 (2008).

8. Miedziak, P.J., S.A. Kondrat., N. Sajjad., G.M. King., M. Douthwaite., G. Shaw., G.L. Brett., J.K. Edwards, D.J. Morgan., G. Hussain, & G.J. Hutchings. Physical mixing of metal acetates: optimisation of catalyst parameters to produce highly active bimetallic catalysts. *Catal. Sci. Technol.* 3: 2910-2917 (2013).

9. Emmanuel S., J.B. Rob., P.S. Vera., G. Jorge., M. Michie., T.K. Michiel., J.K. Patricia., A.M. Jacob, & K. Freek. Inhibition of a Gold-Based Catalyst in Benzyl Alcohol Oxidation: Understanding and Remediation. *Catalysts.* 4: 89-115 (2014).

10. Gergely N., B. Andrea., S. György., S. Zoltán., L. Shaofeng., L. Tianbo., Q. Botao., W. Junhu, & L. Károly. Nanodisperse gold catalysts in oxidation of benzyl alcohol: comparison of various supports under different conditions. *Reac. Kinet. Mech. Cat.* 128: 71-95 (2019).

11. Enache, D.I., D.W. Knight, & G.J. Hutchings. Solvent-free oxidation of primary alcohols to aldehydes using supported gold catalysts. *Catal. Letters,* 103: 43-52 (2005).

12. Enache, D.I., J.K. Edwards., P. Landon., B. Solsona-Espriu., A.F. Carley., A. Herzing., M. Watanabe., C.J. Kiely., D.W. Knight, & G.J Hutchings. Solvent-free oxidation of primary alcohols to aldehydes using Au-Pd/TiO2 catalysts. *Science*, 311: 362-365 (2006).

13. Edwards, J.K., B.E. Solsona., P. Landon., A.F. Carley., A. Herzing., C.J. Kiely, & G.J. Hutchings. Direct synthesis of hydrogen peroxide from H2 and O2 using TiO2-supported Au–Pd catalysts. *J. Catal.* 236: 69-79 (2005).

14. Enache, D.I., D. Barker., J.K. Edwards., S.H. Taylor., D.W. Knight., A.F. Carley, & G.J. Hutchings. Solvent-free oxidation of benzyl alcohol using titania-supported gold–palladium catalysts: Effect of Au–Pd ratio on catalytic performance. *Catal. Today*. 122: 407-411 (2007).

15. Kondrat, S.A., G. Shaw., S.J. Freakley., Q. He., J. Hampton., J.K. Edwards., P.J. Miedziak., T.E. Davies., A.F. Carley., S.H. Taylor., C.J. Kiely, & G.J. Hutchings. Physical mixing of metal acetates: a simple, scalable method to produce active chloride free bimetallic catalysts. *Chemical Sciences* 3: 2965-2971 (2012).

16. Meenakshisundaram, S., E. Nowicka., P.J. Miedziak., G.L. Brett., R.L. Jenkins., N. Dimitratos., S.H. Taylor., D.W. Knight., D. Bethell, & G.J. Hutchings, Oxidation of alcohols using supported gold and gold-palladium nanoparticles. *Farad. Discus.* 145: 341-356 (2010).