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Solvent-free oxidation of benzyl alcohol with oxygen using zeolite-supported Au and Au–Pd catalysts

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The oxidation of benzyl alcohol to benzaldehyde has been investigated in the absence of solvent using zeolite-supported Au and Au–Pd catalysts. Three zeolites were investigated, ZSM-5, zeolite β and zeolite Y, and these were contrasted with the titanoslicalite TS-1 and TiO_2 as supports. For the Au catalysts the best results are obtained with zeolite β as the support and the conversions were comparable or better than those observed with TiO_2 in terms of turn over frequencies. However, the selectivities observed with the acidic zeolites were lower than the non-acidic TS-1 and TiO_2. This is due to the subsequent reaction of benzaldehyde via acid catalysed reactions to give benzyl benzoate and its dibenzyl acetal, and, in some cases dibenzylether. Initial catalysts were evaluated with a gold loading of 2 wt% and increasing this to 4 wt% showed the expected increase in activity, indicating that there is scope to improve the performance of these catalysts. The most active catalysts were prepared by impregnation and catalysts prepared by deposition precipitation were considerably less active. Introduction of Pd into the catalyst improved the activity without significantly affecting the selectivity.

KEY WORDS: gold catalysis; benzyl alcohol oxidation; benzaldehyde.

1. Introduction

Selective oxidation remains an important topic for research. This is due to the importance of selective oxidation as a unit process in the manufacture of chemical intermediates [1]. The oxidation of alcohols to aldehydes is a fundamentally important laboratory and commercial procedure [1–8] since the products are valuable both as intermediates as well as being high-value components for the perfumery industry [1,9,10]. Many selective oxidation reactions are carried out without the use of modern catalytic technology and in such cases these oxidations are effected using stoichiometric oxygen donors, such as chromate or permanganate. However, such reagents are expensive and have serious toxicity issues associated with them [1,9,11–14].

In previous studies, Au nanocrystals have been shown to be highly effective for the oxidation of alcohols with O_2 in aqueous base, in particular diols and triols, but under these conditions the product is the corresponding mono-acid not the aldehyde [15–18]. Gold catalysts have, however, been found effective for the gas-phase oxidation of volatile alcohols to the corresponding aldehydes and ketones [19]. We have also shown that supported gold catalysts can oxidise a range of alcohols using solvent free conditions and in particular we showed that the support played a significant role in subsequent reactions of the reactant and products via aldol type reactions [20].

Subsequently, two studies have shown that supported metal nanoparticles can be very effective catalysts for the oxidation of alcohols to aldehydes using O_2 under relatively mild conditions. Kaneda and co-workers [6] found that hydroxyapatite-supported Pd nanoclusters (Pd/HAP) give very high turnover frequencies (TOFs) for the oxidation of 1-phenylethanol and benzyl alcohol but show limited activity for the oxidation of primary alkyl alcohols, such as octan-1-ol. Corma and co-workers [21] have shown that the addition of Au nanocrystals to CeO_2 converts the oxide from a stoichiometric oxidant to a catalytic system with TOFs similar to those obtained by Kaneda and co-workers [6]. Here the nanocrystalline nature of the support was crucial for the catalysis observed, and Corma and co-workers have shown that this catalyst is very effective for CO oxidation as well [22,23].

Recently, we have shown that supported Au–Pd alloys are efficient catalysts for the direct synthesis of H_2O_2 from H_2 oxidation by O_2 at low temperatures [24–27]. In particular, Au–Pd/TiO_2 catalysts were very selective for H_2O_2 synthesis. Hydroperoxy species are considered to be involved in this H_2O_2 formation process, and because hydroperoxy species are key reagents/intermediates in the oxidation of alcohols [1], we reasoned that these catalysts should also be effective for the oxidation of alcohols. In our very recent paper [28] we reported that TiO_2-supported Au–Pd alloy nanocrystals

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give significantly enhanced activity for alcohol oxidation using a green chemistry approach with O_2 under mild, solvent-free conditions. In particular when the Au–Pd/TiO_2 was compared with mono-metallic supported Au [21] and Pd [6], the Au–Pd catalysts nanocrystals give TOFs enhanced by a factor of ~25.

In this paper we extend the study of using supported Au and Au–Pd catalysts for the oxidation of benzyl alcohol and compare zeolitic supports with TiO_2 for this reaction.

2. Experimental

2.1. Catalyst preparation

Supported catalysts were prepared using impregnation via an incipient wetness method using an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (Johnson Matthey) with nominal gold loadings of 2.0 and 2.5 wt%. For the 2.0 wt% Au-supported catalyst, the detailed procedure was as follows. An aqueous solution of $HAuCl_4 \cdot 3H_2O$ (10 mL of a solution containing 5 g $HAuCl_4 \cdot 3H_2O$ dissolved in 250 mL water) was added to the support (3.8 g). Five supports were used namely, zeolite HZSM-5 (Grace ZL5201, $SiO_2/Al_2O_3 = 45$, total surface area 424 m^2/g), zeolite USY (Grace ZL5100, $SiO_2/Al_2O_3 = 6$, total surface area 760 m^2/g) and zeolite β (Grace, $SiO_2/Al_2O_3 = 166$). The paste formed was ground and dried at 95 °C for 16 h and then also calcined (400 °C) in static air for 3 h. Further catalysts containing different amounts of Au were also prepared using a similar procedure. Catalysts containing Pd were obtained in a similar way, using the required amount of $PdCl_2$ as precursor.

For the 2 wt% Au-supported catalysts obtained via the deposition–precipitation (d.p.) method, the detailed procedure was as follows. Aqueous solution (3.3 mL) of $HAuCl_4 \cdot 3H_2O$ (2 g) dissolved in water (100 mL), was added to distilled water (75.9 mL), urea (2.1 g)and the zeolite support (1.56 g). The mixture was heated to 80 °C and maintained at that temperature for 4 h with stirring. The solid was filtered and washed using distilled water. The paste formed was dried at 90 °C for 16 h and calcined at 300 °C in static air for 3 h.

TiO_2 (P25) support, mainly anatase, with a BET surface area of 50 m^2/g was obtained from Degussa and used as received.

TS-1 ($SiO_2/TiO_2 = 30$) was prepared according to the method of Taramasso *et al.* [29]. Tetraethyl orthotitanate (3 g, Aldrich) was added dropwise to tetraethyl orthosilicate (91 g Merck) and the mixture was stirred for 2 h. To the clear solution, tetrapropylammonium hydroxide (100 g Alfa, 40% in water, K < 1 ppm, Na < 3 ppm) and deionised water (60 g) were added with stirring at 25 °C. The resulting clear gel was stirred at 25 °C for 1 h and then heated at 80 °C for 5 h to aid hydrolysis; during the procedure, the volume was maintained by addition of deionised water. The resulting solution was heated in a teflon-lined stainless steel autoclave at 175 °C for 10 days. The crystalline material was recovered by centrifuging, washed with deionised water, dried at 100 °C, and calcined in air at 550 °C for 24 h. The material was confirmed to be well crystallised TS-1 by powder X-ray diffraction. The total BET surface area was 350 m^2/g.

2.2. Catalyst testing

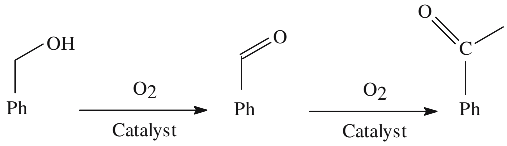
The oxidation reactions were carried out in a 100 mL scale batch stirred reactor (Autoclave Engineers Inline MagneDrive III). The vessel was charged with alcohol (40 mL) and catalyst (0.2 g). The autoclave was then purged five times with oxygen leaving the vessel at the desired pressure (2 bar). The pressure was maintained constant throughout the experiment and so, as the oxygen was consumed in the reaction, it was replenished. The stirrer was set at 1500 rpm and the reaction mixture was raised to the required temperature. Samples from the reactor were taken periodically via a sampling pipe, ensuring that the volume purged before sampling was higher than the tube volume, and analysed by GC using a DB-Wax column.

One of the key factors that must be considered for heterogeneous catalysts operating in three phase systems is the possibility that active components can leach into the reaction mixture, thereby leading to catalyst deactivation or to the formation of an active homogeneous catalyst. Therefore, the final reaction solutions were filtered to remove the particles of catalyst and analysed by atomic absorption spectroscopy to determine the amount of metal leached. No metals constituting the active phase were detected in the filtered reaction mixtures. To check if the catalyst retained its original activity and selectivity, selected catalysts were used for 24 h for the oxidation of benzyl alcohol. The catalysts were recovered by filtration, washed with acetone, and then dried overnight at 80 °C. The recovered powder (0.2 g) was used to perform a new reaction of oxidation of benzyl alcohol for 3 h duration. The experimental results were compared with the results obtained for a fresh catalyst and the results showed no loss of activity and/or selectivity for the re-used catalyst, the differences observed being within experimental error. Hence, we concluded that the catalysts were being tested under conditions where they are effectively heterogeneous catalysts.

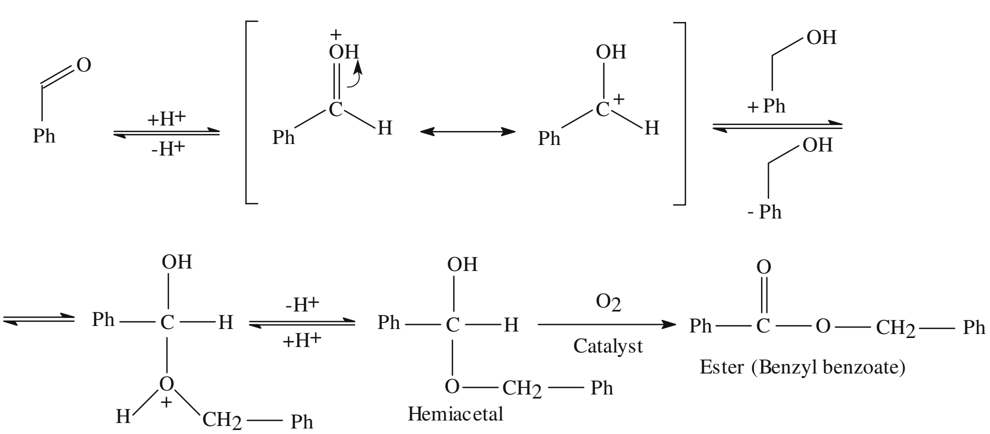
3. Results and discussion

There are a number of products that can be formed by oxidation of benzyl alcohol and it is important to consider these in detail before describing the results we obtained with the zeolite-supported catalysts. The oxidation of benzyl alcohol leads in the first instance to the formation of benzaldehyde, which is the main product during our experiments. Further oxidation of this molecule leads to the production of benzoic acid, as shown in Scheme 1. However, other side reactions are also possible. One pathway is a condensation reaction between the generated aldehyde and the initial alcohol, which is catalysed by the acid–basic sites present on the catalyst (Scheme 2). This generates a hemiacetal, which is unstable under the reaction conditions and is subsequently either oxidised to the corresponding ester (Scheme 2) or, following a subsequent condensation with a second molecule of alcohol, a reaction that is also catalysed by the acid–basic sites of the catalysts, leads to the formation of the corresponding dibenzyl acetal (Scheme 3). Another reaction catalysed by the acid–basic sites of the catalyst leads to the production of dibenzylether (Scheme 4). Finally, there is also the possibility of disproportionation of benzyl alcohol into benzaldehyde, toluene and water (Scheme 5). This last reaction is most probably catalysed by the metallic sites of the catalyst and proceeds by the extraction of the oxygen from the alcohol and subsequently oxidising another molecule of alcohol to aldehyde. This last reaction is favoured by high temperature and low partial pressure of oxygen, and experiments in the absence of oxygen have confirmed this reaction can occur [28].

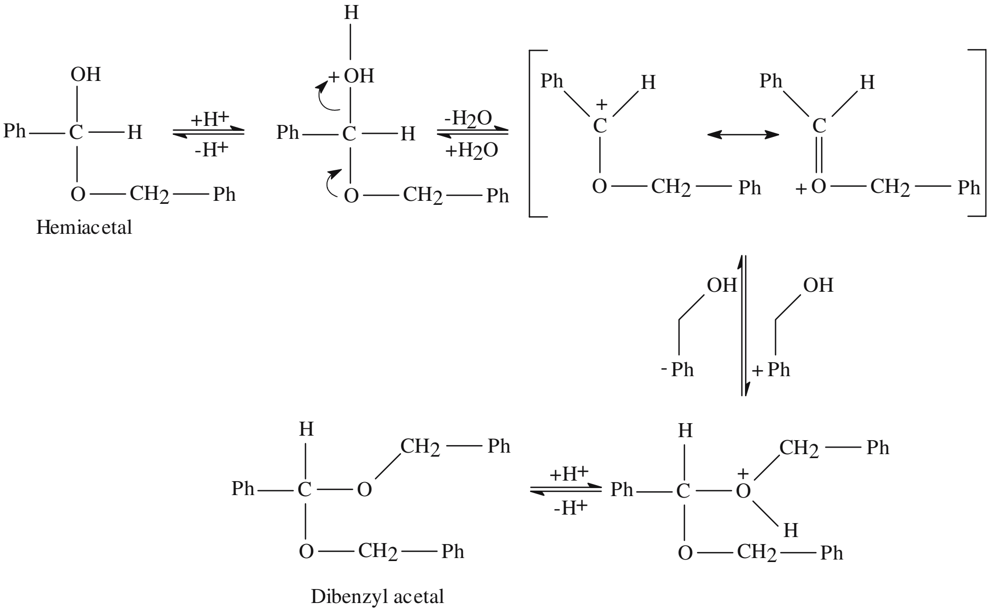
The results presented in table 1 (entries 1–5) show that the activity of the Au catalyst is influenced by the type of support used for the oxidation of benzyl alcohol (see figure 1). The initial activity of the catalysts decreases in the order ZSM-5 > β > Y > TiO_2 > TS-1. For longer reaction time, this order changes, as the catalysts supported on the zeolites Y and β deactivate with reaction time. This deactivation is probably caused by the irreversible chemisorption of certain reaction products, leading to coke formation. A very interesting trend is also observed in the case of the variation in benzaldehyde selectivity with the benzyl alcohol conversion (figure 2). The highest selectivity in benzaldehyde is obtained for the catalyst supported on TiO_2, followed by the catalysts supported on TS-1, ZSM-5 and finally zeolites Y and β. It is interesting to note that the trend for benzaldehyde selectivity is different for the catalysts supported on zeolites compared with other oxide supports. In the case of TiO_2 and TS-1, the selectivity in benzaldehyde decreasing with increasing benzyl alcohol conversion caused by an increase of the reaction time whereas an opposite effect is observed for the case of the catalysts supported on zeolites. In the case of zeolite Y and β-supported catalysts, this behaviour is correlated with the evolution in the selectivity in dibenzylether, which is significant at the beginning of the reaction, but decreases gradually, as the selectivity in benzaldehyde increases. For all other catalysts, including ZSM-5 as a support, the selectivity in dibenzylether is zero at all reaction times, the main by-product in these cases being the acetal product. Another interesting observation concerns the selectivity to toluene. The catalysts supported on TiO_2 and TS-1 give a low level of selectivity in toluene (less than 1–2%), while for the zeolites Y and β as supports, toluene selectivity is in the range 3–5% and for the catalyst supported on ZSM-5, the selectivity in toluene increases to around 14%. All these observations are considered to be consistent with the acidity and the pore size distribution of the supports. Indeed, the higher acidity of the zeolites guides the reaction towards the formation of more substantial quantities of dibenzylether, with the exception of ZSM-5; this is probably due to the pore structure of this zeolite. The catalysts supported on TiO_2 and TS-1 present a higher selectivity for the acetal (*ca.* 10%) when



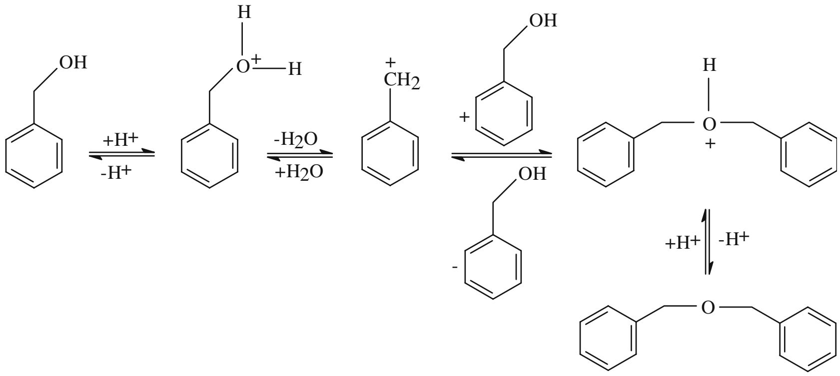
Scheme 1.



Scheme 2.



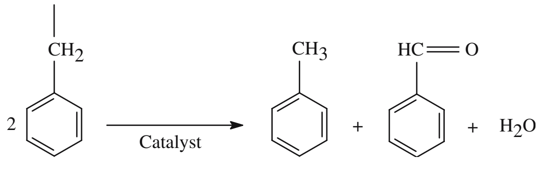
Scheme 3.



Scheme 4.

compared with the zeolites-supported catalysts. This observation indicates that the production of acetal is catalysed by weaker acidic sites than those required for the production of dibenzylether, a mechanistically reasonable conclusion.

The increase of the metal content from 2% Au to 4% Au on zeolite Y and ZSM-5 leads to an increase in the activity of the catalyst, but not by the same factor (figure 3). Although the same method of preparation was employed, the particle size of the metal is expected to increase with the increase of the metal loading and consequently the value of the TOF decreases (table 1, entries 3, 4, 6 and 7). The increase of the metal loading increases the selectivity to benzaldehyde for supports (figure 4), as the amount of dibenzylether is decreased in the case of zeolite Y, while the selectivity in acetal is decreased in the case of the ZSM-5-supported catalyst. For both cases, the selectivity in toluene is slightly increased at higher metal loading. This behaviour can be explained by the higher metal loading leading to an increase in the coverage of the surface of the support and consequently a decrease in the number of acidic sites capable of catalysing these side reactions leading to dibenzyl acetal and/or dibenzylether. However, the increase in metal loading leads to an increase in the selectivity to toluene, which is considered to be related to the increase of the metal surface area.



Scheme 5.

The method of catalyst preparation was also investigated. Two catalysts containing Au supported

Table 1
Oxidation of benzyl alcohol using zeolite-supported catalysts[a]

Entry	Catalyst	Conversion (%)	Au	[Metal] × 10^5 (mol/L)		TOF (h^{-1})
				Au	Pd	
1	2%Au/β	1	1.99	50.8	0	378
2	2%Au/TS-1	1.5	1.33	50.8	0	169
3	2%Au/Y	0.5	0.90	50.8	0	345
4	2%Au/ZSM-5	1	2.59	50.8	0	493
5	2.5%Au/TiO_2	0.5	0.70	63.5	0	213
6	4%Au/Y	0.5	0.89	101.6	0	169
7	4%Au/ZSM-5	1	3.46	101.6	0	329
8	2%Au/Y-dp	1	1.68	50.8	0	321
9	2%Au/ZSM-5-dp	0.5	1.23	50.8	0	468
10	2%Pd/Y	1	2.97	0	94.3	304
11	2%Au-2%Pd/Y	1	4.21	50.8	94.3	280
12	2.5%Au-2.5%Pd/TiO_2	0.5	3.70	63.5	118	394

[a]All reaction were carried out at 100 °C, 2 bar O_2 pressure and 1500 rpm stirrer speed.

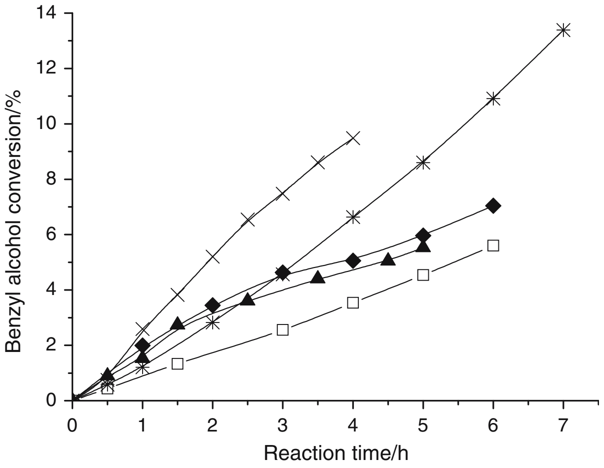


Figure 1. Effect of the support for the benzyl alcohol conversion with the reaction time; (♦) 2%Au/β, (□) 2%Au/TS-1, (▲) 2%Au/Y, (×), 2%Au/ZSM-5, (*) 2.5%Au/TiO_2.

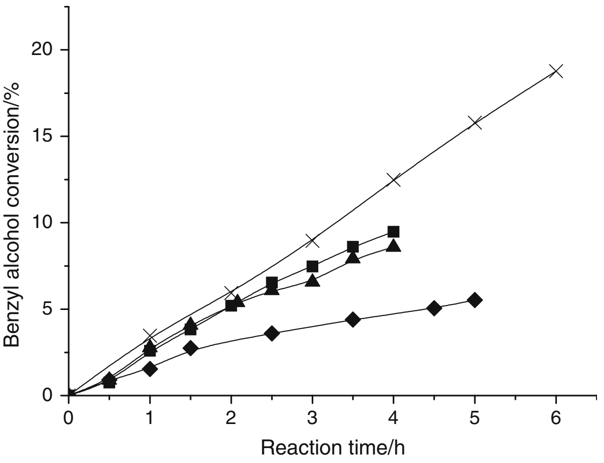


Figure 3. Effect of the metal loading for the benzyl alcohol conversion with the reaction time; (♦) 2%Au/Y, (■) 2%Au/ZSM-5, (▲) 4%Au/Y, (×) 4%Au/ZSM-5.

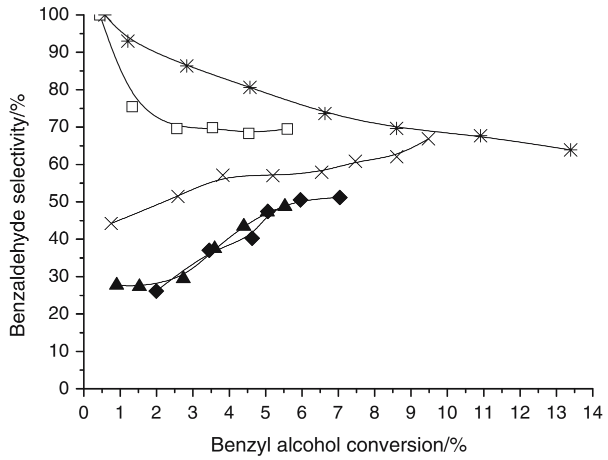


Figure 2. Effect of the support for the benzaldehyde selectivity with the benzyl alcohol conversion; (♦) 2%Au/β, (□) 2%Au/TS-1, (▲) 2%Au/Y, (×) 2%Au/ZSM-5, (*) 2.5%Au/TiO_2.

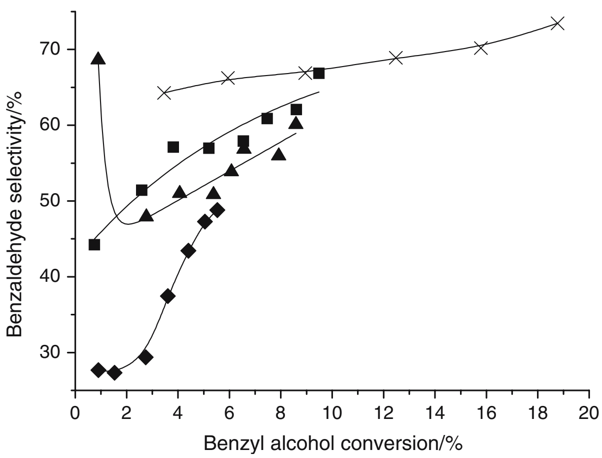


Figure 4. Effect of the metal loading for the benzaldehyde selectivity with the benzyl alcohol conversion; (♦) 2%Au/Y, (■) 2%Au/ZSM-5, (▲) 4%Au/Y, (×) 4%Au/ZSM-5.

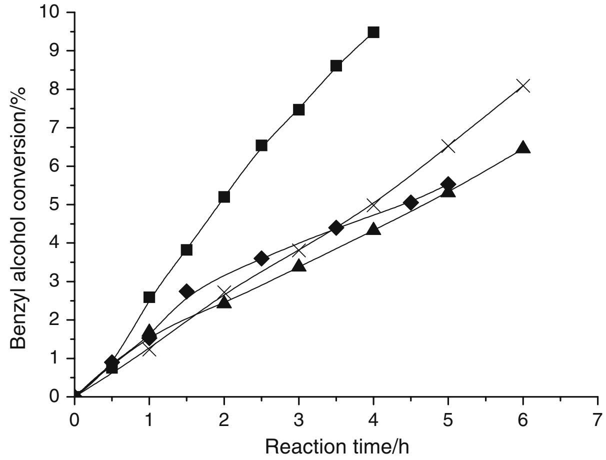


Figure 5. Effect of the preparation method for the benzyl alcohol conversion with the reaction time; (♦) 2%Au/Y, (■) 2%Au/ZSM-5, (▲) 2%Au/Y-d.p., (×) 4%Au/ZSM-5-d.p.

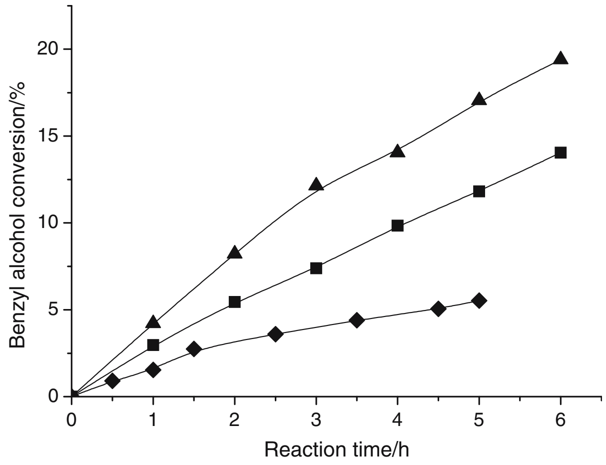


Figure 7. Effect of the metal or alloy for the benzyl alcohol conversion with the reaction time; (♦) 2%Au/Y, (■) 2%Pd/Y, (▲) 2%Au-2%Pd/Y.

on ZSM-5 and zeolite Y were also prepared *via* a deposition–precipitation (d.p.) method and the catalytic results obtained were contrasted with the results obtained with the impregnation method (figure 5). In the case of the catalysts supported on ZSM-5, the catalyst obtained by d.p. method gave a lower activity, while for the zeolite Y-supported catalyst, the activity appears to be influenced to a lesser extent by the preparation method (table 1, entries 3, 4, 8 and 9). However, the catalysts obtained by d.p. gave a higher selectivity to benzaldehyde at iso-conversion, compared with the catalysts obtained from impregnation. This increase in benzaldehyde selectivity is related to a decrease in the selectivity to dibenzylether for the zeolite Y-supported catalyst, while in the case of the ZSM-5-supported sample, a decrease in the selectivity in toluene was observed. We propose that the base used to precipitate the Au precursor during the d.p. preparation procedure neutralises some of the acidic sites of the catalyst, which are responsible for ether production in the case of zeolite Y (see figure 6).

In a final set of experiments was investigated the addition of Pd to Au, which leads to an increase in the activity of the catalyst (figure 7). The activity appears to increase with the addition of Pd to Au, which is consistent with our earlier findings [28]. However, if the activity is related to the total metal present, then the effect is not as marked. TOF values based on total metal content decreased for Au–Pd/zeolite Y. The selectivity to benzaldehyde at iso-conversion is similar for these catalysts and a small increase in selectivity is observed in the order Au < Pd < Au–Pd (see figure 8).

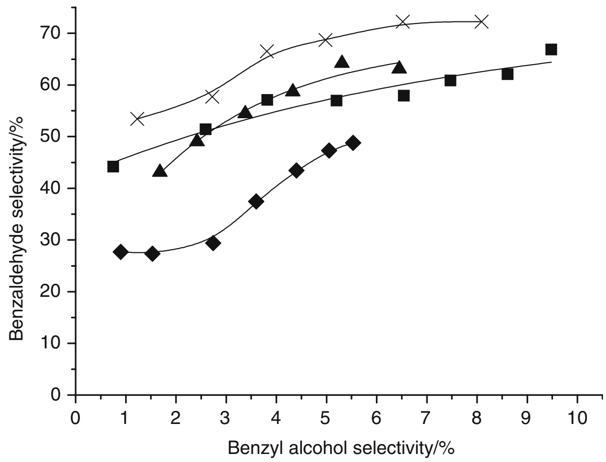


Figure 6. Effect of the preparation method for the benzaldehyde selectivity with the benzyl alcohol conversion; (♦) 2%Au/Y, (■) 2%Au/ZSM-5, (▲) 2%Au/Y-d.p., (×) 4%Au/ZSM-5-d.p.

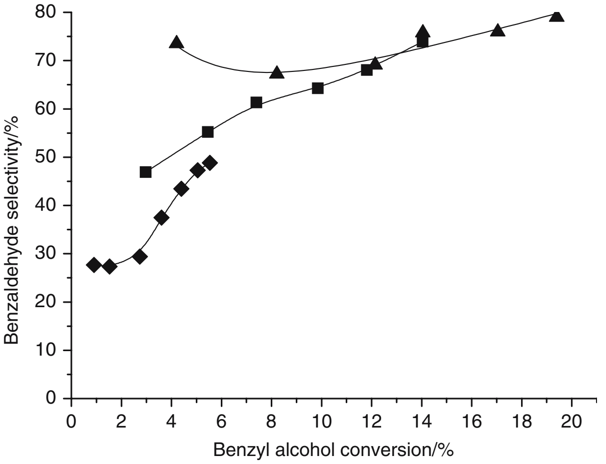


Figure 8. Effect of the metal or alloy for the benzaldehyde selectivity with the benzyl alcohol conversion; (♦) 2%Au/Y, (■) 2%Pd/Y, (▲) 2%Au-2%Pd/Y.

4. Conclusions

Zeolite-supported Au catalysts are effective for the direct oxidation of benzyl alcohol to form benzaldehyde; however, the acidic nature of these supports can catalyse sequential reactions of the reactant and products. The Au-supported catalysts using zeolite β as a support gave turnover frequencies comparable to those observed with TiO_2 in our previous study [28]. The addition of Pd leads to an increase in activity without markedly affecting the selectivity.

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