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Short communication

Acceptorless dehydrogenation of 1-phenylethanol using Pd/TiO_2 catalysts prepared by sol immobilisation



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	Reversible hydrogenation and acceptorless dehydrogenation of organic molecules would enable pre-existing technologies and infrastructure to be leveraged for the storage and transport of hydrogen. We report the synthesis of active Pd/TiO ₂ catalysts prepared by sol immobilisation for the acceptorless dehydrogenation of 1-phenylethanol to acetophenone with evolution of molecular hydrogen. The catalyst converts 1-phenylethanol with a TOF of 3600 mol _{1-PE} h ⁻¹ mol _{Pd} ⁻¹ while maintaining high selectivity (>95%) at over 80% conversion. This represents a 3.5 x increase in catalytic activity with comparable selectivity over commercially available 5% Pd/C catalysts.			

1. Introduction

The conversion of alcohols to carbonyls *via* oxidation has been extensively studied due to the importance of ketones and aldehydes in biomass conversion [1] and fine chemical synthesis. [2] This is often achieved synthetically using stoichiometric oxidants such as potassium dichromate; however this produces significant amounts of waste. Catalytic oxidation using molecular O₂ has been extensively developed [3], however poor control of autoxidation and unselective reaction pathways can produce undesired products through radical reaction pathways. [4] Acceptorless alcohol dehydrogenation (AAD) is a potential technology to convert alcohols to carbonyls releasing molecular H₂. This makes AAD attractive not only in the synthesis of molecules such as oxalamides [5] and esters [6] through dehydrogenative coupling but also has potential for cyclic hydrogenation-dehydrogenation reactions as a H₂ storage mechanism.

To date, the development of AAD has focused on homogeneous Ru systems, such as the work of Milstein in dehydrogenative coupling of polyols and amino alcohols with pincer catalysts. [7] However, homogeneous catalysis requires extensive separation procedures. In addition, high reaction temperatures require molecular catalysts to be stable under such conditions in the presence of H₂. Heterogeneous catalysts are preferable for H₂ storage applications due to their high thermal stability and ease of separation from the reaction mixture, limiting downstream processing. To date, the field of liquid organic hydrogen carriers

(LOHCs) has developed (de)hydrogenation of cyclic alkanes and aromatics. [8] This is achieved using supported Pd, Pt and Ni catalysts at high temperature and pressures, the potential of this first generation LOHC technology has recently been realised be establishing a 4000 km H₂ supply chain between Brunei and Japan based on toluenemethylcyclohexane hydrogenation-dehydrogenation. [9]

Alongside the production of molecular H_2 , efficient catalysts are required to supress the hydrogenolysis of the C—O bond and dehydration of the alcohol group to form alkenes which are subsequently hydrogenated removing C—O functionality. For this reason, high selectivity is key in maintaining a closed cycle for the efficient storage and release of H_2 . Pd has been shown to be an effective catalyst with interest also in metallic Pt, Au, Ag, Ru, Ni, Cu, and Co particles. [10–18] Metals such as Cu are viewed as cheaper and more abundant replacements for noble metals, however large metal :substrate ratios are often required and catalysts can become passivated by surface oxidation. [14] For this reason Pd and Pt remain the most studied metals for this process with cyclic alkanes.

Shimizu and co-workers proposed that AAD occurred at the metalsupport interface in their Ni/ θ -Al₂O₃ system. The amphoteric nature of the θ -Al₂O₃ was thought to increase activity compared to more acidic or basic supports. The effect of varying nanoparticle size was also investigated for this system, the turnover frequency per surface metal was seen to increase as nanoparticle size decreased suggesting the possible importance of metal-support interfaces. [16] Similar observations were

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made by Chen and co-workers, who observed that by decreasing the size of Au nanoparticles supported on hydrotalcite activity increased. It was also noted that the selectivity was unaffected by the nanoparticle size. [18]

While the use of Pd is very well established for hydrogenations; given the limited abundance of Pd, there is a significant drive to optimize such catalysts to limit the amount of Pd required and maximise activity. [10] Commercial Pd/C catalysts studied in recent literature for the dehydrogenation of 1-phenylethanol (1-PE) were shown to have high selectivity (>97%) towards acetophenone (AP) in an open system. The selectivity decreased significantly when the reaction was performed in a closed system, suggesting the build-up of H₂ promoted the hydrogenolysis of 1-phenylethanol to produce ethylbenzene (EB), preventing regeneration of the starting product *via* hydrogenation. In this work, the performance of a Pd/TiO₂ catalyst made using sol immobilisation was studied for the acceptorless dehydrogenation of 1-phenylethanol to produce acetophenone and molecular H₂.

2. Experimental details

Catalyst synthesis - Catalysts (Pd/TiO₂) were prepared by colloidal methods as has been previously reported using PVA as the stabilising polymer (PVA:Pd = 1: 1.2 (wt/wt)) and NaBH₄ as the reducing agent (NaBH₄:Pd 5: 1 (mol/mol)). [19,20] Detailed preparation methods are reported in the SI. Commercial catalysts were obtained from Sigma Aldrich and used without any further treatment. Catalyst Testing - 1-phenylethanol was used as a model substrate for acceptorless dehydrogenation reactions - typically 1-phenylethanol in xylene (10 mL, 0.4 M) was reacted at 120 °C under flowing Ar with 20 mg catalyst to give a nominal Pd mol% of 0.05. The reaction solution was analysed by GC after set time intervals, typically 30, 60, 90, 120 mins using biphenyl as an external standard. Full details of dehydrogenation and subsequent hydrogenation reactions can be found in the SI. Catalyst Characterisation - Catalysts were characterised by XPS, TEM, and ICP-MS to determine structural characteristics. Full experimental details can be found in the SI.

3. Results and discussion

Recently Hammond et al. demonstrated for the first time that commercial 5% Pd/C could be an effective catalyst for 1-phenylethanol dehydrogenation to acetophenone with high selectivity (>98%) and TOF 1475 h⁻¹. Analysis of this commercial catalyst by TEM suggested that while the mean particle size is small (3.5 nm) there are significantly larger particles present (up to 10 nm) potentially reducing the effective use of PGMs. Colloidal catalyst preparation methods allow Pd catalysts to be prepared with tight particle size distributions between 3 and 5 nm to increase precious metal utilisation. Fig. 1 compares 1-phenylethanol dehydrogenation activity of a commercial 5% Pd/C with a 1% Pd/C prepared by colloidal methods with identical Pd mol%. Both catalysts were active, reaching conversions of 78% and 75% respectively at 120 mins (TOFs of 1000 and 940 mol mol_{Pd}^{-1} h⁻¹ determined after 30 min reaction). Iso-conversion comparison of selectivity from the reaction was 96% and 89% towards the dehydrogenation product acetophenone. The lower observed selectivity in the colloidally prepared catalyst could be a result of the acidification during catalyst preparation resulting in surface acid groups on the carbon. Huang and co-workers showed by ATR studies that acidic sites promoted 1-phenylethanol dehydration forming styrene which is hydrogenated to ethylbenzene over the Pd catalyst. [21] Using less acidic catalyst supports such as TiO₂ could supress this unselective reaction. We prepared an analogous 1% Pd/TiO₂ catalyst and tested it under identical conditions to the carbon supported samples (Fig. 1). The catalyst demonstrated higher activity than the 5% Pd/C catalyst while crucially retaining high selectivity (96% at 80% conversion) at similar conversion to the colloidally prepared 1% Pd/C, ethylbenzene was the minor reaction product (4% selectivity).



Fig. 1. Conversion (solid line) and selectivity (dotted line) of 1-phenylethanol dehydrogenation as a function of time comparing commercial 5% Pd/C to as prepared 1% Pd/TiO₂ and 1% Pd/C at 0.05 Pd mol%. 120 °C, 1000 rpm, 0.355 M 1-PE, flowing Ar, 20.9 mg (1% Pd/TiO₂, 1% Pd/C) / 5.4 mg (5% Pd/C) catalyst.

A key consideration is to ensure that the reaction is truly acceptorless and stoichiometric release of H₂ can be observed. A series of experiments were conducted in a sealed glass vessel to measure the volume of H₂ evolved by an inverted burette method. Due to the reversibility of the cyclic (de)hydrogenation, equilibrium limits the conversion of 1-phenylethanol to ~22% in a closed system, therefore we conducted experiments for fixed times with increasing amounts of catalyst (1–20 mg). Fig. 2 shows good agreement between the conversion measured by GC analysis and the conversion determined by H₂ volume measurements indicating the reaction is truly acceptorless. Approaching equilibrium conversion with higher Pd mol% some deviation is seen due to H₂ being



Fig. 2. Conversion as a function of Pd mol% in a closed system under Ar atmosphere, conversions calculated from both the volume of gas evolved from the reaction and GC analysis.

in the system for extended times with the substrates leading to side reactions. The high catalyst loading leads to C-OH bond cleavage consuming H_2 , despite this, side reactions were minimal at low conversions meaning that with effective H_2 removal near quantitative H_2 evolution is possible while producing carbonyl compounds from alcohols.

As ethylbenzene was produced with high catalyst loadings in a closed system, we investigated the initial stages of the reaction in an open system with Ar purging. Heating to the desired temperature without stirring could produce high localised H₂ concentrations at the catalyst surface if the reaction begins in a poor mass transfer regime. We carried out a reaction by adding the catalyst and reagents, purging with inert gas and heating to reaction temperature (15 mins of equilibration), assuming the reaction is initiated by stirring following the equilibration. [10] In this reaction system, gas purging was achieved by in/out flow through the same port (the borosilicate dip tube of a 10 mL glass reactor). We observed approximately 11% conversion and 50% selectivity to ethylbenzene during the 15-min temperature equilibration (Fig. 3) when the catalyst is not being agitated. Carrying out the reaction in this way resulted in a selectivity towards acetophenone of 74% and a conversion of 54% after 2 h. To prevent any reaction occurring whilst the temperature was equilibrating, an analogous experiment was carried out, but the catalyst was added after the equilibration as the reaction was stirred with separate gas in and out ports to aid H2 removal (2 neck flask with condenser). This increased the selectivity to 96% and conversion to 74% over 2 h. The increase in ethylbenzene production suggests mass transport effects play a significant role in selectivity (and conversion via hydrogenation of produced acetophenone). Without agitation, H₂ can only diffuse slowly away from the catalyst surface, meaning a greater concentration of H2 available for hydrogenolysis and the production of ethylbenzene. This optimised method was used for all subsequent work and indicates that many studies' reported data could be a result of experimental method and poor mass transfer in the initial stages.

Three catalysts prepared in the same way with different nominal metal loadings (0.5%, 1.0%, and 2.0%) were tested for the dehydrogenation of 1-PE with details shown in Table 1 (Entry 1–3). ICP analysis was used to accurately determine the Pd loadings, in all cases the Pd loadings were significantly lower than our targets, resulting in increased mass normalised activity of the 1 wt% Pd/TiO₂ tested in Fig. 1 in comparison to the commercial 5 wt% Pd/C (3,600 vs 1000 mol_{1-PE} h⁻¹



Fig. 3. Conversion (solid line) and selectivity (dotted line) as a function of time for two different methods, adding catalyst at different times. $120 \,^{\circ}$ C, $1000 \,$ rpm, flowing Ar, $20 \,$ mg catalyst (1% Pd/TiO₂).

Table 1

Catalytic Activities of Synthesised Pd/TiO₂ catalysts for AAD of 1-Phenylethanol - 120 °C, 1000 rpm, 0.355 M 1-PE, flowing Ar, 20.9 mg (1% Pd/TiO₂, 1% Pd/C) / 5.4 mg (5% Pd/C) catalyst. All heat treatments were 3 h.

Entry	Nominal Pd Loading / wt %	Heat Treatment	Conversion at 2 h / %	Selectivity / %	ICP / wt%
1	0.5	-	41	100	0.17
2	1.0	-	82	96	0.36
3	2.0	-	86	96	0.60
4	1% Pd/C	-	75	89	-
5	5% Pd/C ^b	-	78	96	5.0 ^b
6	1.0 _N ₂	-	91	94	0.84
7	1.0 ^a	300 $^\circ \text{C}$ / air	76	96	-
8	1.0 ^a	400 °C / air	81	97	-
9	1.0 ^a	500 °C / air	59	95	-
10	1.0 ^a	300 °C / Ar	71	95	-
11	1.0 ^a	400 °C / Ar	62	95	-
12	1.0 ^a	500 °C / Ar	71	95	-

^a Derived from nominal 1.0 wt% loading – actual loading 0.36 wt%.

 $^{\rm b}$ Commercial Pd/C obtained from Sigma Aldrich with 5.0 wt% certified loading.

 ${\rm mol}_{\rm Pd}^{-1}$ at 30 mins reaction). Across the three metal loadings reactivity obeys simple first order kinetics with similar k_{obs} (when normalised to Pd loading) suggesting only minimal changes in the Pd speciation as loading is varied which is expected when using the colloidal preparation method (Fig. S2a-b). A possible reason for this discrepancy is the reoxidation and dissolution of colloidal metallic Pd particles while stirring under ambient conditions during our preparation. To probe this, we conducted a catalyst preparation while purging the solution with N₂-the loading of this catalyst (0.84 wt%) determined by ICP was much closer to the nominal target of 1 wt% and provided an effective catalyst for the acceptorless dehydrogenation reaction, reaching conversions of over 90% in 2 h with similar kinetics. This suggests that metallic Pd catalysts can be effectively prepared by colloidal methods by removing the oxidative atmosphere, in contrast to bimetallic catalysts which do not require such control of the environment.

Stability of the 1 wt% Pd/TiO $_2$ was assessed using heat treatment and hot filtration studies. Characterisation of the fresh material by TEM (Fig. 4) showed that the material consisted of Pd nanoparticles with mean particle size 3.6 \pm 0.8 nm consistent with the reports of Dimitratos [22] and Villa [23] for catalysts prepared in this manner. XPS analysis of the Pd 3d region (Fig. S3a) of fresh catalyst indicated the presence of both Pd^0 and Pd^{2+} (77% Pd^0), suggesting surface oxidation on storage of the samples. TEM of the catalyst after 2 h of reaction showed a mean particle size of 4.4 \pm 1.5 nm, suggesting a small amount of sintering occurs during the reaction. These observations are consistent with a reduced Pd: Ti atomic ratio as measured by XPS (fresh 0.016 vs used 0.013). Used catalyst TEM images (Fig. S4) also showed amorphous material around the Pd particles suggesting that the PVA has remained on the catalyst surface during reaction - PVA has limited solubility in the reaction solvent. XPS analysis of the used sample (Fig. S3b) showed only Pd^0 suggesting that H_2 produced on the catalyst surface from the dehydrogenation of 1-phenylethanol reduced any surface PdO present during the reaction. The presence and subsequent reduction of PdO does not seem to have any effect on the dehydrogenation reaction. An experiment was performed in which catalyst was pre-reduced with a 5% $\mathrm{H_2/N_2}$ gas mix in-situ. The conversion over 2 h using that catalyst matched that of experiments performed without a pre-reduced catalyst. A hot filtration was performed to ensure no homogeneous catalysis occurred because of metal leaching into the solution. After 30 min the catalyst was filtered from a dehydrogenation reaction and the filtrate left to stir at reaction conditions for a further hour. No further reaction was observed, confirming that the reaction is occurring only at the catalyst surface. In addition to chemical stability, the thermal stability of the Pd catalyst was investigated in both air and Ar between 300 and



Fig. 4. (left) Hot filtration study on 1% Pd/TiO₂. 120 °C, 1000 rpm, flowing Ar, 20 mg catalyst. (right) Distribution of Pd nanoparticle diameters before and after use in a dehydrogenation reaction, measured from TEM images.

500 °C (Table 1). Catalyst samples treated under Ar were found to have only slightly reduced activity, dropping from 82% conversion over 2 h (fresh catalyst) to around 70% with minimal mass loss detected by TGA consistent with polymer removal at these treatment temperatures (Fig. S5). Samples treated in air maintained similar conversions to that of the untreated catalyst up to 400 °C, after which the conversion dropped to 59% consistent with a mass loss and combustion of the stabilising polymer at this temperature. In all cases the treated catalyst samples maintained selectivities of around 95% and the relative stability of the samples under elevated temperature and inert atmospheres suggest gas phase dehydrogenation could be achieved with these materials.

One application of AAD in addition to the synthesis of carbonyl compounds is the development of LOHCs. To effectively load and unload H₂ from these carrier molecules the catalyst must be able to selectively cycle through dehydrogenation and hydrogenation reactions with little to no loss of carbonyl/alcohol functionality. 1-phenylethanol is a model compound to probe this cyclic de(hydrogenation) and activity of catalysts towards unselective reactions in both hydrogenation and dehydrogenation conditions which has a theoretical H₂ loading of 1.8 wt%, below the US Department of Energy target of interim 5.5 wt% for on board hydrogen use in fuel cell vehicles but can serve as a useful model. [24] Preliminary cycling experiments were carried out on the 1-phenylethanol - acetophenone system, using our 1% Pd/TiO₂ catalyst. As can be seen in Fig. 5, Pd/TiO₂ was able to effectively catalyse both (de)hydrogenation reactions by changing the atmosphere in the reaction vessel from Ar (1 bar) to H₂ (3 bar) to cycle between 1-phenylethanol and acetophenone. Inspection of results over the 4 cycles suggests the catalyst maintains similar rates for each step. Over the course of 4 (de)hydrogenation cycles there is an accumulation of ethylbenzene - final selectivity 10%. As the product of non-reversible hydrogenolysis in both reactions, the formation of ethylbenzene results in a loss of molecules with the functionality to undertake further (de)hydrogenation cycles. Our results show that most ethylbenzene is formed during the hydrogenation steps of the cycle and identifying the catalyst features to minimise this reaction pathway will be the subject of future studies.

4. Conclusions

 Pd/TiO_2 catalysts were synthesised using sol immobilisation methods and tested for the acceptorless dehydrogenation of 1-phenylethanol, producing acetophenone and ethylbenzene, along with



Fig. 5. Selectivity as a function of time for EB, AP, and 1-PE, as the reaction conditions are cycled between hydrogenation (120 $^{\circ}$ C, 650 rpm, 3 bar H₂) and dehydrogenation (120 $^{\circ}$ C, 1000 rpm, flowing Ar) 1% Pd/TiO₂ (20 mg).

quantitative volumes of H₂. High selectivity towards acetophenone (>95%) was observed over the 2 h reaction period, with TOFs of ~3600 mol_{1-PE} h⁻¹ mol_{Pd}⁻¹, representing a 3.6× increase compared to commercial 5% Pd/C catalysts with comparable selectivity. The catalyst retained similar conversions and selectivity to un-treated samples when heated to temperatures greater than 400 °C in both air and Ar. The potential for Pd/TiO₂ catalysts to be used for H₂ storage was demonstrated by cycling between hydrogenation and dehydrogenation conditions, the catalyst being active for both reactions.

Author credit statement

Hannah Rogers and Isaac Daniels - Catalyst Synthesis, Testing,

Characterisation, *Simon Freakley* – Research concept and direction. All authors contributed to writing, editing, and revising the paper.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2021.106377.

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