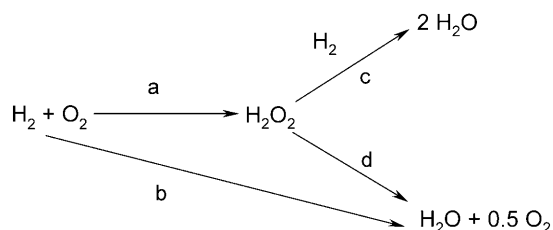


Direct Synthesis of H_2O_2 from H_2 and O_2 over Gold, Palladium, and Gold–Palladium Catalysts Supported on Acid-Pretreated TiO_2 **

Jennifer K. Edwards, Edwin Ntainjua N, Albert F. Carley, Andrew A. Herzing, Christopher J. Kiely, and Graham J. Hutchings*

Hydrogen peroxide is a major commodity chemical produced currently by using an indirect process. A direct process (Scheme 1, path a) would be preferred and palladium cata-



Scheme 1. Formation and decomposition pathways for hydrogen peroxide. a) Formation, b) combustion, c) hydrogenation, and d) decomposition.

lysts^[2–5] have demonstrated catalytic activity for such a process; recently we have shown that the addition of gold to palladium improves the catalyst performance.^[6–8] The major problem associated with the direct synthesis of H_2O_2 is the decomposition (Scheme 1, path d) or hydrogenation (Scheme 1, path c) of H_2O_2 by the catalysts used for its formation.

To overcome the problem of these sequential reactions with palladium catalysts stabilizers are required;^[3,5] these are typically mineral acids and halides. However, the presence of stabilizers in the reaction medium pose serious problems

since they have to be removed from the product after the reaction, especially when the effluent H_2O_2 is to be used without refinement (e.g., epoxidation of propylene). We have found that for Au–Pd catalysts the addition of a halide and acid promoters is not required.^[9] However, H_2 selectivities for these catalysts are at best 80% under typical reaction conditions, which involve reactions at sub-ambient temperatures (ca. 2°C).^[7] Improvements in selectivity are now required so that the catalysts can be used at higher temperatures without loss of performance.

Herein we show that the pretreatment of a TiO_2 support with acid prior to the addition of the metals leads to a catalyst which gives improved selectivity and activity. We have previously shown that for a carbon-supported Au–Pd catalyst, the acidic pretreatment^[8] results in an increase in the activity for the direct synthesis of hydrogen peroxide. Most importantly, we show herein for the first time that the methodology is not only applicable to metal-oxide-supported catalysts, but can be used at ambient temperature with enhanced catalyst performance; the untreated catalysts cannot be used at these temperatures.

Gold, palladium, and gold–palladium catalysts supported on TiO_2 were prepared by using wet impregnation. We also investigated the effect of acidic pretreatment of the TiO_2 prior to the impregnation of the metals onto the support (see the Supporting Information). This pretreatment step consists of suspending TiO_2 in a 2 wt % aqueous HNO_3 solution for three hours and subsequent washing (thoroughly with approximately 1 L H_2O) and then drying (120°C). After calcination (400°C) the pretreated Au–Pd/ TiO_2 was more active and more selective for the direct synthesis of H_2O_2 as compared with the untreated catalyst (compare entries 2 and 8 in Table 1). To evaluate whether the aqueous nature of the pretreatment solution was responsible for the improved catalyst activity, the catalyst was prepared using TiO_2 which had simply been subjected to a water treatment (i.e., no aqueous HNO_3 solution). This catalyst exhibited the same activity and selectivity (Table 1, entry 5), based on the conversion of H_2 into H_2O_2 , as the catalyst prepared with untreated TiO_2 (Table 1, entry 2). A similar observation was made in the cases of the supported monometallic gold and palladium catalysts when the catalytic activities of catalysts supported upon untreated and water-pretreated TiO_2 were compared (compare entries 1 and 4 and entries 3 and 6 in Table 1). Interestingly, the activity of the monometallic Au and Pd catalyst remained unchanged regardless of acidic pretreatment of the TiO_2 support (compare entries 1 and 7, and entries 3 and 9 in Table 1), indicating that the improvement is observed only for the bimetallic catalyst. For the acid-

[*] Dr. J. K. Edwards, Dr. E. Ntainjua N, Dr. A. F. Carley, Prof. G. J. Hutchings
Cardiff Catalysis Institute, School of Chemistry, Cardiff University
Main Building, Park Place, Cardiff, CF10 3AT (UK)

Dr. A. A. Herzing,^[†] Prof. C. J. Kiely
Center for Advanced Materials and Nanotechnology
Lehigh University
5 East Packer Avenue, Bethlehem, PA 18015-3195 (USA)

[†] Current address: National Institute of Standards and Technology,
Surface and Microanalysis Science Division
100 Bureau Drive, stop 8371, Gaithersburg, MD 20899-8371 (USA)

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Table 1: Activity and selectivity of TiO₂-supported catalysts for H₂O₂ synthesis at 2 °C.

Entry	Catalyst ^[a]	Pretreatment ^[b]	Selectivity [%] ^[c]	Productivity [mol h ⁻¹ kg _{cat} ⁻¹]
1	5 % Au/TiO ₂	none	n.d.	7
2	2.5 % Au–2.5 % Pd/TiO ₂	none	70	64
3	5 % Pd/TiO ₂	none	21	30
4	5 % Au/TiO ₂	water	n.d.	7
5	2.5 % Au–2.5 % Pd/TiO ₂	water	70	64
6	5 % Pd/TiO ₂	water	21	31
7	5 % Au/TiO ₂	2 % HNO ₃	n.d.	8
8	2.5 % Au–2.5 % Pd/TiO ₂	2 % HNO ₃	95	110
9	5 % Pd/TiO ₂	2 % HNO ₃	22	33

[a] Metal loadings denoted as mass fractions. All catalysts were calcined in air at 400 °C for 3 h. Reaction conditions: catalyst (10 mg), 2.9 MPa H₂ (5 % volume fraction)/CO₂ and 1.1 MPa O₂ (25 % volume fraction)/CO₂, 2 °C, 0.5 h, methanol/water (5.6 g methanol, 2.9 g water) as solvent. [b] Acid concentration expressed in terms of volume fraction; pretreated as indicated for 3 h (see the Supporting Information for details). [c] n.d. = not determined; the conversion was too low for reliable data.

pretreated Au–Pd/TiO₂ catalyst, the H₂ selectivity is increased to approximately 95 %, which represents a significant improvement over the H₂ selectivity of approximately 70 % observed with the untreated catalyst (compare entries 2 and 8 in Table 1). We initially considered this enhancement in H₂ selectivity to be the result of a decrease in the rate of sequential hydrogenation/decomposition of H₂O₂. However, H₂O₂ hydrogenation/decomposition were not significantly affected by the pretreatment process (see Table 1 in the Supporting Information), representing a distinct and important difference between the catalysts on acid-pretreated TiO₂ supports and those on acid-pretreated carbon supports, which we have been previously reported.^[8] The treatment of the carbon support leads to the complete suppression of the H₂O₂ decomposition/hydrogenation reaction. Nevertheless, despite this difference in behavior, the pretreatment with acid still gives a profound enhancement in the performance of the Au–Pd/TiO₂ catalysts which must be a result of an increase in the rate of synthesis of H₂O₂.

The calcined acid-pretreated catalysts could be reused several times (Figure 1 a) without any loss of performance. After each standard reaction the catalyst was recovered and dried in air (120 °C). For each use, the acid-pretreated catalyst gave an activity of 110 mol H₂O₂ kg_{cat}⁻¹ h⁻¹ as determined after 30 minutes of reaction, with 30 % hydrogen conversion. Interestingly, the addition of nitric acid to the reaction mixture prior to initiating H₂O₂ synthesis (which is an established procedure for stabilizing H₂O₂,^[10] as H₂O₂ decomposition is known to be a base-catalyzed process) also led to an enhancement in the yield of H₂O₂, but the effect was not sustained upon subsequent catalyst reuse (Figure 1 a). Treatment of the support after metal deposition did not enhance catalyst performance and neither did the addition of nitric or hydrochloric acid during the metal impregnation step. These results demonstrate that the precise sequence in which the acidic pretreatment is carried out is crucial. However, neither the acid concentration nor the duration of the acidic pretreatment are considered to be critical to observe this effect.

In an additional set of experiments we examined the effect of the reaction temperature on H₂O₂ productivity (Figure 1 b) and it is apparent that the acid-pretreated catalysts can be

successfully used at ambient temperature. We consider this improvement to result from the enhanced selectivity, which is based upon H₂ usage with the acid-pretreated catalysts. Indeed, even at 40 °C the pretreated Au–Pd/TiO₂ catalyst retains higher activity than the untreated catalyst at 2 °C. In contrast, the untreated catalysts show a steady decrease in product yield as the temperature is increased.

To gain an insight into the cause of the performance improvement observed we have analyzed the catalysts using elemental analysis, electron microscopy, and X-ray photoelectron spectroscopy (XPS).

ICP-MS showed that the acidic pretreatment of the support did decrease the levels of impurities in TiO₂ (see the

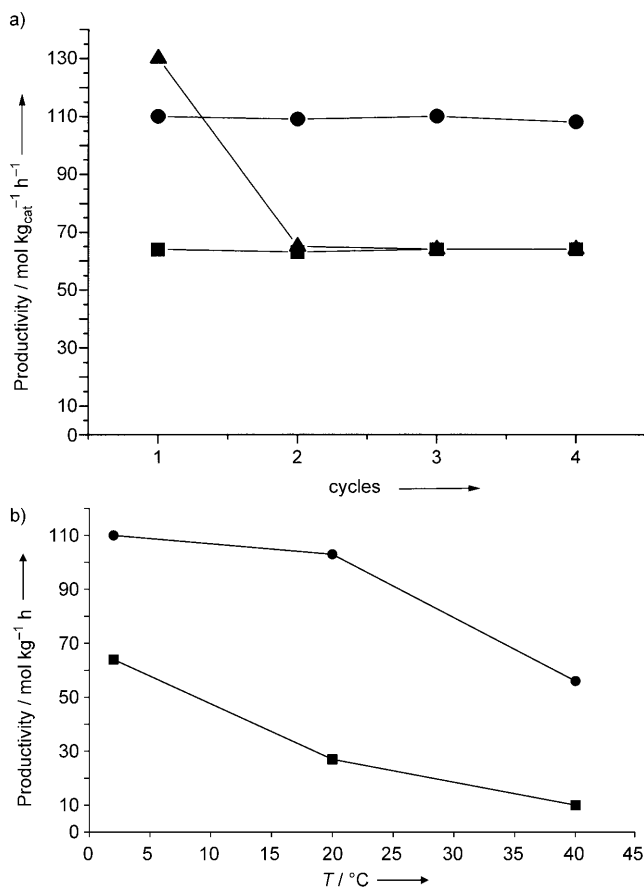


Figure 1. Performance of acid-pretreated Au–Pd/TiO₂ catalysts for the synthesis of H₂O₂ compared with untreated Au–Pd/TiO₂ catalysts. a) The untreated (■) and 2 % HNO₃ treated (●) Au–Pd/TiO₂ catalysts are stable over four cycles, with the latter showing a higher activity. The addition of 2 % HNO₃ to a solution of the untreated Au–Pd/TiO₂ catalyst (▲) in the autoclave, shows a higher initial activity compared to the untreated catalyst. This higher activity is lost upon subsequent reuse, attaining the same catalytic activity level as that of the untreated catalyst. b) The effect of reaction temperature on the performance of the untreated (■) and 2 % HNO₃ treated (●) Au–Pd/TiO₂ catalysts.

Supporting Information). Bright-field electron microscopy shows that the catalyst comprises a broad distribution of nanoparticles (Figures 2a and b). However, by comparison (Figure 2c) the acidic pretreatment of the TiO_2 support removes the larger particles and reduces the average Au–Pd particle size. We have previously shown that the Au–Pd alloy

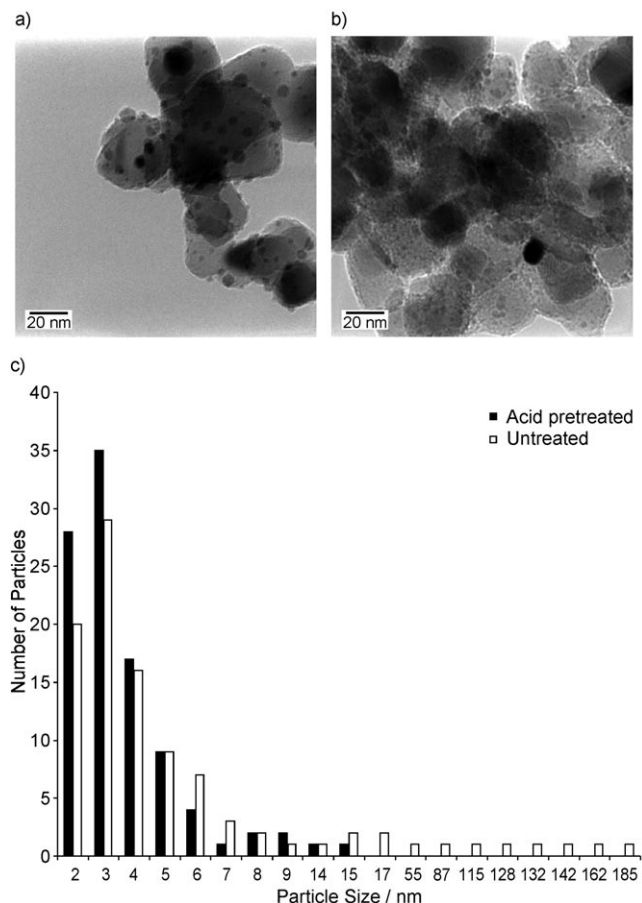


Figure 2. Representative bright field micrographs of a) the untreated and b) the acid-pretreated Au–Pd/TiO₂ samples. c) Comparison of the particle size distributions of the untreated and pretreated Au–Pd/TiO₂ samples.

particles in these catalysts show a systematic correlation between particle size and composition, with the larger particles being more gold-rich and the smaller ones being more palladium-rich.^[11,12] A low magnification annular dark-field (ADF) image and corresponding Au–L_α and Pd–L_α X-ray energy dispersive spectra (XEDS) elemental maps obtained from the acid-pretreated AuPd/TiO₂ sample (see Figure S2 in the Supporting Information) show a similar correlation between particle size and composition as was noted previously for conventional the untreated sample.^[11,12] Hence the shift to smaller average particle sizes for the acid-pretreated TiO₂ substrate is an indication that the gold is being more efficiently dispersed and alloyed during the impregnation step as compared to that of its untreated counterpart.

When supported on TiO₂, the Au–Pd alloy particles with sizes as small as approximately 6 nm are known from our previous studies^[11,13,14] to develop a gold-rich core and palladium-rich shell structure during the 400 °C calcination step. Because of the spatial resolution limits of our XEDS spectrum imaging technique, we cannot discriminate if particles below approximately 6 nm in size also have the same core–shell morphology. Figure 3 shows an ADF image

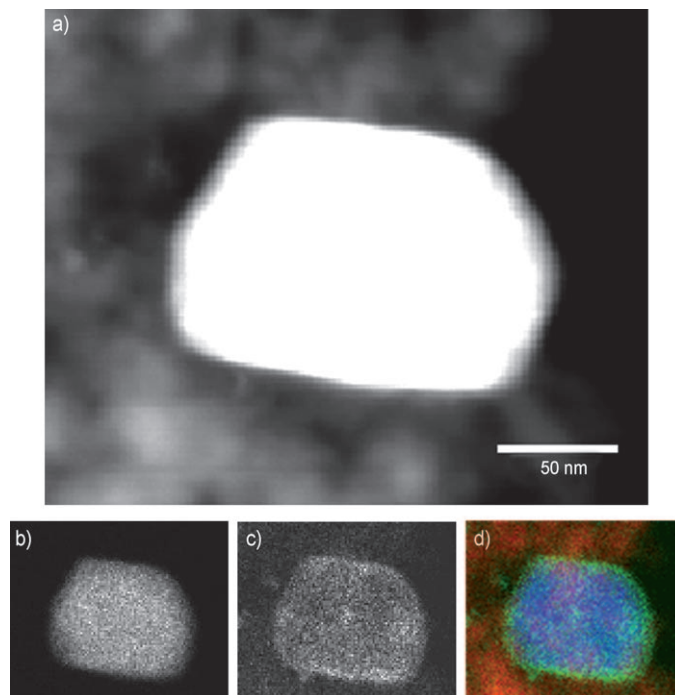


Figure 3. An ADF image (a) and the corresponding Au–L_α (b), Pd–L_α (c), and Ti–Au–Pd overlay (d) elemental maps of one of the largest particles found in the acid-pretreated Au–Pd/TiO₂ catalyst sample. Together they reveal a definite gold-rich core–palladium-rich shell morphology.

and the corresponding elemental XEDS maps from one of the larger bimetallic particles in the acid-pretreated catalyst sample, which clearly demonstrate that an gold-rich core–palladium-rich shell morphology is once again present. Hence we consider that the acidic pretreatment of the TiO₂ support does not significantly alter the propensity of the Au–Pd particles to develop core–shell structures upon calcination.

We have also examined the untreated and acid-pretreated titania supports using XPS methods to elucidate the nature of any changes induced by the acidic pretreatment of the support (see the Supporting Information). The surface concentrations of gold and palladium for the acid-pretreated support are increased compared with the untreated materials, which is in agreement with the increased metal dispersion indicated by the STEM-XEDS. An XPS spectrum of the pretreated support, compared to that of the untreated support, shows changes in the peaks associated with the O, N, Cl, indicating the nature of the oxide surface has changed. These observed changes together with the removal of impurities can be anticipated to play a role in the dispersion of the metals.

On the basis of these analyses it is clear that the acidic pretreatment does not affect the core-shell morphology of the Au-Pd alloy nanoparticles and the catalysts supported on both the pretreated and untreated supports have nanoparticle surfaces which are palladium enriched. This palladium-enriched surface possibly accounts for the observation that the acidic pretreatment does not switch off the sequential H_2O_2 hydrogenation/decomposition reactions, which we did previously observe for the pretreated carbon-supported Au-Pd catalysts which do not have palladium-enriched surfaces.^[8] Palladium catalysts are known to be highly active for such sequential reactions^[2,15] and with the core-shell morphology the gold has a more limited effect when compared with homogeneous alloy nanoparticles. It is possible that the acidic pretreatment may affect the surface acidity especially at the sites adjacent to the core-shell alloy nanoparticles. However, at this stage we consider the effect of the acidic pretreatment of the support is to enhance the dispersion of gold within the catalyst, leading to an increased proportion of smaller Au-Pd nanoparticles. This effect may be induced by changes in the surface composition with respect to oxygen and halide features. It is this shift in particle size distribution that enhances the activity of the catalysts and enables them to be useable at higher temperatures.

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