

Direct formation of hydrogen peroxide from H₂/O₂ using a gold catalyst

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Received (in Cambridge, UK) 29th May 2002, Accepted 1st August 2002

First published as an Advance Article on the web 14th August 2002

Supported Au catalysts are very selective for the direct formation of hydrogen peroxide from H₂/O₂ mixtures at 2 °C; the rate of H₂O₂ synthesis is markedly increased if Au–Pd alloy nanoparticles are generated by the addition of Pd.

Selective oxidation is important in the synthesis of fine chemicals and intermediates.¹ Recently, there has been much interest in the design of new heterogeneous catalysts for selective oxidation under ambient conditions, and these typically use hydrogen peroxide as the oxidant.^{2,3} At present, hydrogen peroxide is produced by the sequential hydrogenation and oxidation of alkyl anthraquinone⁴ and global production is ca. 1.9 × 10⁶ tonnes per annum. This process is currently only economic on a large scale (4–6 × 10⁴ tpa), whereas it is often required practically on a much smaller scale. In view of this, there is considerable interest in the direct manufacture of hydrogen peroxide from the catalysed reaction of hydrogen and oxygen.^{5,6} At present, some success has been achieved using Pd as a catalyst, especially when halides are used as promoters.^{7,8} Typically, dilute solutions of hydrogen peroxide are produced, and earlier studies indicate that the Pd catalyst can be combined with an oxidation catalyst, TS-1, so that the hydrogen peroxide produced is used *in situ*.⁹ A further recent development in catalysis has been the marked interest in using supported Au as an active oxidation¹⁰ and hydrogenation catalyst,¹¹ and very recently we have been shown that Au supported on carbon can selectively oxidise glycerol to glyceric acid.¹² Supported Au catalysts have been investigated for the oxidation of propene to propene oxide using O₂/H₂ mixtures,¹³ and it is considered that a surface hydroperoxy species may be formed as the oxidant. To date, there are no reported studies concerning the use of supported Au catalysts for the direct synthesis of hydrogen peroxide from O₂/H₂. We have now addressed this point and, in this communication, we show that supported Au catalysts can be very effective and, furthermore, the rate of hydrogen peroxide formation can be significantly enhanced by the use of a supported Au/Pd alloy.

Our initial approach to the design of a direct hydrogen oxidation process for the synthesis of hydrogen peroxide, was to use supercritical CO₂ as a reaction medium. This is because earlier studies with Pd catalysts have indicated that H₂ diffusion is a significant problem and this can be expected to be largely

overcome by using supercritical media due to the enhanced solubility of H₂.¹⁴ Au/ZnO, Pd/ZnO and Au:Pd/ZnO catalysts containing 5 wt% metal were prepared by coprecipitation.¹⁵ These catalysts were evaluated for the synthesis of hydrogen peroxide using supercritical CO₂ (35 °C, 9.7 MPa) using a standard procedure.¹⁶ The results are shown in Table 1 and it is apparent that the Au/ZnO and Au:Pd/ZnO catalysts exhibit some hydrogen peroxide synthesis, albeit at a low rate. However, the Pd catalyst only generated water as a product. At this temperature it was considered that the hydrogen peroxide formed was relatively unstable with respect to decomposition or hydrogenation (see Scheme 1). This was confirmed in a separate experiment in which H₂O₂ (16.8 × 10⁻⁵ mol, 0.5 wt%) was stirred with and without the Pd catalyst under the same conditions in supercritical CO₂. When the Pd catalyst was present ca. 30% of the hydrogen peroxide decomposed in 1 h and, even in the absence of a catalyst, ca 10% was decomposed. Hence, although using supercritical CO₂ as the reaction medium may have overcome the diffusion limitation, the inherent instability of hydrogen peroxide at the elevated temperature required to achieve supercritical conditions mitigates against the use of this medium.

Subsequently, experiments were conducted at significantly lower temperatures (2 °C) and the results, also shown in Table 1, indicate that hydrogen peroxide can be formed at a high rate for the supported Au catalyst. The selectivity for H₂O₂ for the Au/Al₂O₃ catalyst was determined to be 53%. In this case, the catalysts were prepared by impregnation¹⁷ and they were tested

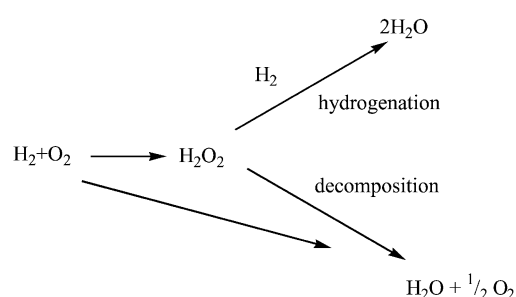


Table 1 Formation of H₂O₂ from the reaction of H₂/O₂ over Au and Pd catalysts

Catalyst	Solvent ^a	Temperature/ °C	Pressure/ MPa	O ₂ /H ₂ mol ratio	H ₂ O ₂ ^b mmol g(catalyst) ⁻¹ h ⁻¹
Au/Al ₂ O ₃	CH ₃ OH	2	3.7	1.2	1530
Au:Pd (1:1)/Al ₂ O ₃	CH ₃ OH	2	3.7	1.2	4460
Pd/Al ₂ O ₃	CH ₃ OH	2	3.7	1.2	370
Au/ZnO	SCCO ₂	35	9.2	1.0	9
Au:Pd (1:3)/ZnO	SCCO ₂	35	9.2	1.1	7
Au:Pd (1:1)/ZnO	SCCO ₂	35	9.2	0.8	12
Au:Pd (3:1)/ZnO	SCCO ₂	35	9.2	0.9	8
Pd/ZnO	SCCO ₂	35	9.2	1.3	0

^a SCCO₂ = supercritical CO₂, details of experimental methods given in refs. 16 and 18 ^b Rate of H₂O₂ formation averaged over 30 min experiment.

for hydrogen peroxide formation at 2 °C using methanol as solvent.¹⁸ The supported Au catalyst produces more hydrogen peroxide than the supported Pd catalyst. However, more interestingly, the supported Au:Pd (1:1 by wt) catalyst produces significantly more than the pure Au catalyst. This indicates a synergistic effect of Pd acting as a promoter for the Au catalyst. To demonstrate that the supported gold catalysts functioned as wholly heterogeneous catalysts, an experiment was carried out using a supported gold catalyst at 2 °C and the yield of H₂O₂ was determined. Following this reaction, the gold catalyst was removed by careful filtration and the solution was used for a second experiment using O₂/H₂. No further H₂O₂ was formed and this confirms that the formation of hydrogen peroxide involves gold acting as a wholly heterogeneous catalyst. To determine if the supported Au: Pd catalyst comprise AuPd alloy particles or if the two components exist separately, the material was examined by scanning transmission electron microscopy (STEM) as shown in Fig. 1.¹⁹ In the bright field image (top left) it is difficult to distinguish the metal particles from the Al₂O₃ support. However, the annular dark field image (top right) gives strong atomic number (Z) contrast and shows the metal particles as bright spots which range from 2 to 9 nm in diameter. Energy dispersive X-ray (EDS) maps of the same area using the Al K_α (1.486 eV) O K_α (0.525 eV), Au L (9.712 eV) and Pd L (2.838 eV) signals are also shown as a montage in Fig. 1. It is clear that the Au and Pd signals are spatially superimposed indicating that the metal nanoparticles are in fact AuPd alloys. EDS point analysis from more than 200 particles have been carried out which show that all the particles are alloys and although there is some compositional variation from particle-to-particle, the average composition is 50 wt% Au:50 wt% Pd as expected.

This study demonstrates that supported Au catalysts are effective for the direct synthesis of hydrogen peroxide from hydrogen and oxygen. In particular, Au catalysts may provide a significant improvement over Pd catalysts that have been investigated previously.^{4–9} At the present time, it is not possible to comment on whether the improved hydrogen peroxide yield

observed with the Au catalysts results from either a decrease in the rate of H₂O₂ decomposition or an enhancement in the rate of H₂O₂ formation and this will be the subject of further study.

This work formed part of a research project set up and executed under the Institute of Applied Catalysis Foresight Challenge Research Programme and we thank the Institute of Applied Catalysis and the EPSRC for funding.

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- 15 Au/ZnO, Pd/ZnO and Au-Pd/ZnO catalysts containing 5 wt% metal were prepared by co-precipitation. An aqueous solution of Pd(NO₃)₂·6H₂O (Strem, 99.999%) and/or HAuCl₄·3H₂O (Strem, 99.9%) and Zn(NO₃)₂·H₂O (Aldrich, 99.999%) which contained the calculated amounts of Pd and/or Au to give the desired loading on ZnO was heated to 80 °C. Na₂CO₃ (Aldrich, 1 mol l⁻¹) was added with stirring, until pH 9 was reached and the mixture was stirred for a further 45 min. The catalyst was washed with hot deionised water and recovered by filtration, dried at 120 °C and calcined (400 °C; 3 h) and then reduced in a flow of 5% H₂ in Au at 400 °C.
- 16 Catalyst testing was carried out in a Parr stainless steel autoclave with a nominal volume of 50 ml. Typically the catalyst was charged with catalyst (0.05 g), solvent, purged three times with CO₂ (3 MPa) and then filled with 5% H₂/CO₂ and 25% O₂/CO₂ to give the required O₂/H₂ ratio. For the experiments in supercritical CO₂, additional CO₂ was then added to a total pressure of 9.2 MPa using a Milton Roy dosing pump. The reaction mixture was stirred (1200 rpm) at 35 °C for 1 h. H₂ and O₂ were analysed by on-line gas chromatography and H₂O₂ was determined at the end of the experiment using a titration method with Ce(SO₄)₂.
- 17 Au/Al₂O₃, Pd/Al₂O₃ and Au:Pd/Al₂O₃, catalysts containing 5 wt% metal were prepared using incipient wetness impregnation of γ-Al₂O₃ (Condea SCF-140) with Pd(NO₃)₂·6H₂O (Strem, 99.999%) and/or HAuCl₄·3H₂O (Strem 99.9%). The catalysts were dried, calcined and reduced as specified in ref. 15.
- 18 Experiments were carried out at 2 °C using aqueous methanol (CH₃OH, 5.6 g; H₂O, 2.9 g) as solvent as otherwise described in ref. 16.
- 19 Samples were analysed in a VG systems HB601 UX scanning transmission electron microscope operating at 100 kV. The microscope was fitted with an Oxford Instruments INCA TEM 300 system for energy dispersive X-ray (EDS) analysis. Samples for STEM examination were prepared by dispersing the catalyst powder in high purity ethanol, then allowing a drop of the suspension to evaporate on a holey carbon microscope grid.

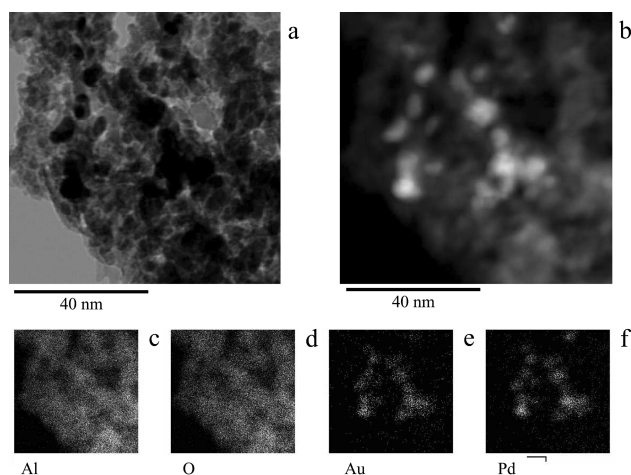


Fig. 1 Bright field (top left) and annular dark field (top right) STEM images of the Au Pd/Al₂O₃ catalyst. The lower montage shows a series of X-ray maps of the same area taken with Al K_α, O K_α, Au L and Pd L signals.