TS-1 Supported Precious Metal Catalysts for the Direct Synthesis of Hydrogen Peroxide

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Abstract:

We demonstrate high catalytic activity towards hydrogen peroxide (H_2O_2) generated from molecular H_2 and O_2 using Au-Pd-Pt trimetallic catalysts supported on a commercial titanium silicate (TS-1). H_2O_2 generation via the direct combination of H_2 and O_2 presents an attractive and atom efficient route to an important commodity chemical removing the financial and environmental drawbacks associated with the Anthraquinone Oxidation (AO) process, the current industrial process for H_2O_2 synthesis.

Keywords: Hydrogen Peroxide, Gold-Palladium, Direct Synthesis

1. Introduction

Hydrogen peroxide is an important commodity chemical, used primarily as a bleaching agent or disinfectant. In addition the high oxygen content and 'green' credentials of H_2O_2 has accounted for an increasing interest in its use as an oxidant for chemical synthesis. Titanium silicate-1 (TS-1) has widely been reported to offer high selectivity and efficiency in oxidation reactions alongside pre-formed H_2O_2, with the catalytic conversion of propylene to propylene oxide a key industrial process[1]. A significant cost to this process is incurred from the production, concentration, transportation and dilution of H_2O_2, which can be overcome via producing H_2O_2 at source. In this contribution we show that the H_2O_2 can be produced by supporting trimetallic nanoparticles on the titanium silicate to form a composite catalyst for H_2O_2 generation.

2. Experimental

Catalyst Preparation.

0.66 wt. % Au-Pd and Au-Pd-Pt catalysts supported on a commercial TS-1 have been prepared by a wet impregnation procedure that is scalable to industrial requirements, using $PdCl_2$, H_2PtCl_6 and $HAuCl_4.3H_2O$ as metal precursors. Catalysts were dried and ground prior to calcination in static air, to produce stable and reusable catalysts.

Direct synthesis of H_2O_2.

Hydrogen peroxide synthesis was evaluated using a Parr Instruments stainless steel autoclave with a nominal volume of 100 ml and a maximum working pressure of 14 MPa. To test each catalyst for H_2O_2 synthesis, the autoclave was charged with catalyst, solvent (MeOH and H_2O). The autoclave was with 5% H_2 / CO_2, followed by the addition of 25 % O_2 / CO_2 to give a hydrogen to oxygen ratio of 1 : 2 and a total pressure of 4.0 MPa. The temperature was then decreased to 2 ^{O}C followed by stirring of the reaction mixture for 30 min. H_2O_2productivity was determined by titrating aliquots of the final solution after reaction with acidified $Ce(SO_4)_2$ (0.01 M) in the presence of ferroin indicator.

3. Results and discussion

Low loaded Au-Pd catalysts supported on a commercial TS-1 are shown to offer high yields of cyclohexanone oxime, via the in-situ synthesis of H_2O_2 from molecular H_2 and O_2. A small addition of Pd to monometallic Au resulted in a significant increase H_2O_2 synthesis activity, as seen previously when these catalysts have been prepared on common oxide supports.

With the addition of a small amount of Pt catalyst selectivity towards H_2O_2, under our standard reaction conditions, improves and an enhancement in the rate of H_2O_2 synthesis is seen, from 44 to 56 $mol_{H2O2}kg_{cat}^{-1}h^{-1}$. With this value comparable to that observed for the well studied 5 % AuPd / TiO_2 catalyst[2], despite much lower metal loadings. We ascribe the increase in catalytic activity with Pt addition to an increase in the Pd : Au surface ratio, as derived from XPS analysis. We report an increase in the Pd : Au surface ratio upon incorporation of 0.11 wt. % Pt, with a similar enhancement reported previously for Au-Pd catalysts supported on CeO_2[3] and TiO_2[4]. This effect can be attributed to the enhancement of the core-shell morphology via the addition of Pt or by a higher dispersion of Pd rich particles on the surface of the TS-1 support.

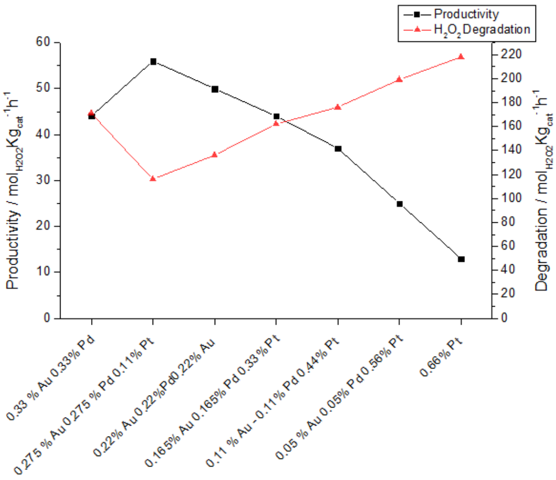

Figure 1. The effect of Pt addition to AuPd / TS-1 on catalytic activity towards H_2O_2 synthesis and its subsequent degradation.

4. Conclusions

We have demonstrated that it is possible to achieve significantly high yields of H_2O_2, a key commodity chemical for a range of chemical syntheses. The talk will focus on the relationship between catalyst composition and activity towards the direct synthesis of H_2O_2, with particular interest in the potential application of in-situ generated H_2O_2 as an oxidisng agent when used alongside TS-1.

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