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RESEARCH PAPER

An insight into the superior performance of a gold nanocatalyst on single wall carbon nanotubes to that on titanium dioxide and amorphous carbon for the green aerobic oxidation of aromatic alcohols

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Abstract: Gold nanocomposites based on three supports, single wall carbon nanotubes, carbon black and TiO_2, were prepared using an in-situ reduction technique and characterized. They were tested for their suitability as heterogeneous catalysts in the green aerobic oxidation of 1-phenylethanol, 2-phenylethanol and benzylalcohol of industrial importance. For all reactions, the use of single wall carbon nanotubes as supports resulted in superior reaction efficiency and specificity for aldehyde to that of TiO_2 and carbon black. The gold nanocatalysts can be reused over several reaction cycles with a minimal degeneration in catalytic activity. The activity of the gold nanoparticle catalyst was related to the shape and size of the gold particles and the properties of the support. The selectivity was ascribed to the functional groups on the substrate, the properties of the supports and the particle size distributions of the gold nanoparticles.

Key Words: Aromatic; Alcohols; Gold; Nanocatalysts; Selectivity

1 Introduction

The use of nano gold particles (Au NPs) as an active phase in catalysis has taken off enormously since Haruta's pioneering work in the area in 1989 [1]. Since then there has been a myriad of publications highlighting the high catalytic activity and selectivity in a large number of oxidation reactions of industrial importance, including the oxidation of glucose [2], alcohols [3] and polyols, most specifically glycerol[4].

The oxidation of alcohols to their corresponding aldehydes or ketones is seen as one of the simplest and most useful transformations in organic chemistry and is at the core of an array of synthetic routes in industrial chemistry [5]. Thus, the ability to catalyse these reactions under more 'green' conditions is highly desirable. Of concern is that most of the catalysts or processes that have been identified to date are relatively inactive for primary alkyl or secondary alcohols and those used generate heavy-metal waste. In addition, they are generally run using chlorinated solvents or acidified systems [6, 7]. From a green point of view, using O_2 as an oxidant under atmospheric conditions in place of stoichiometric oxygen donors would be ideal, as H_2O would be the only by-product of the process. Nevertheless, using O_2 does raise safety concerns, particularly at high temperature and pressure, and so it is preferable to be able to use oxygen at atmospheric pressure.

Typically, catalyst systems used for these types of reactions require the use of solvents, so it is pertinent that the development of catalysts that can operate in a solventless system be explored in a drive to improve environmental friendliness. In addition, in order to endeavour to stay within the rigors of 'green' processes, it is necessary to either minimise or, whenever possible, eliminate the production of heavy metal or chlorinated waste generated during the reactions. Hence, a system in which the only by-product is water would potentially be a significant development of catalytic processes in industrial chemistry. Primary aromatic (benzylic) alcohols can be readily transformed to aldehydes that are relatively resistant to further oxidation, at least under mild conditions [8]. An example of this is the oxidation of benzyl alcohol (phenylmethanol), which is one of the most commonly reported test reactions and has been characterised extensively showing excellent selectivities and yields on almost all common catalysts [9].

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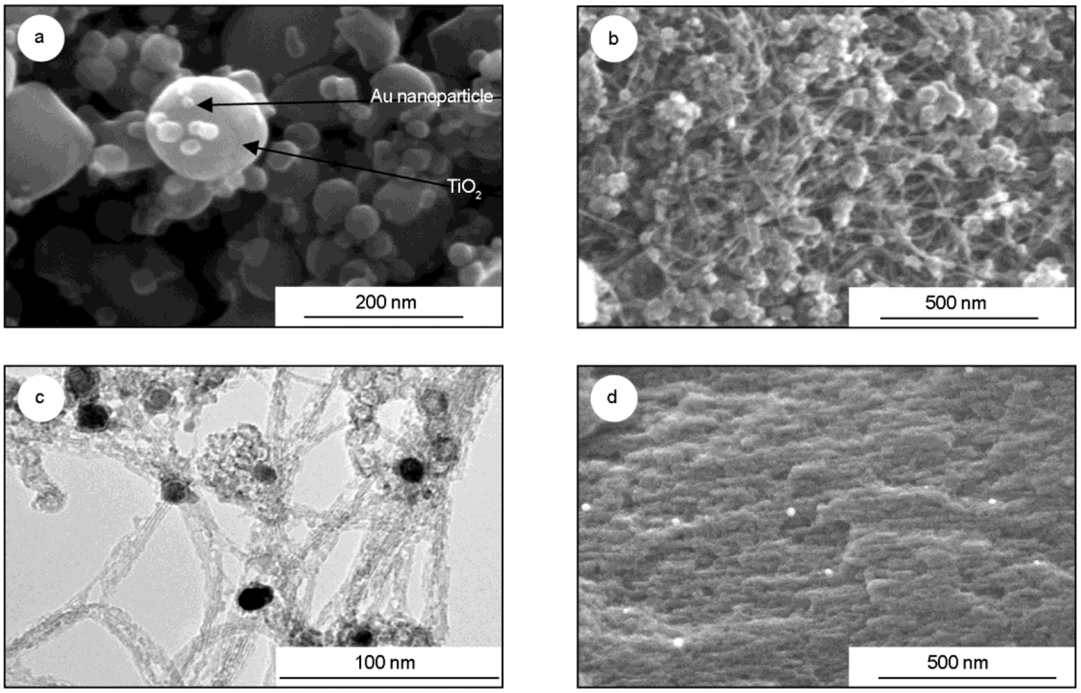

Fig. 1 SEM/TEM images of (a) Au/TiO_2, (b) SWCNT, (c) Au/SWCNT and (d) Au/P90

However, there are very few probe reactions commonly used to compare different types of catalysts for the selective transformation of alcohol to aldehyde/ketone and/or carboxylic acid [10]. Also, more often than not, further oxidation of aldehydes to their corresponding acids is considered to be an undesirable side reaction and thus catalysts and processes are regularly optimised to avoid it. In a previous paper, we described the catalytic potential of Au/SWCNT for the liquid phase oxidation of 1-phenylethanol to acetophenone [11]. This work highlighted a preliminary use for SWCNT as a catalyst support in a 'green' reaction.

The object of this follow on work was to compare three supported gold nano composites as catalysts in the aerobic oxidation of three aromatic alcohols (one secondary and two primary) used as probe reactions and offer some insight into the role of the support materials in the selectivity of the catalysts themselves.

2 Experimental

Titanium IV dioxide nanopowder and the SWCNT used in this work were sourced from Sigma-Aldrich. In the case of the SWCNT, prepared by the so-called Arc-Discharge Method[12], the reported composition is ~70% SWCNT (with single tube diameters between 1.2-1.5 nm and bundles of lengths in the order of ~20μm), ~30% amorphous carbon and ≤ 1% nickel/yttrium [13]. The carbon black (P90) whose chemical composition is amorphous carbon was gifted by Degussa. Gold chloride ($HAuCl_4$) and sodium borohydride ($NaBH_4$) were also sourced from Sigma-Aldrich. Finally, doubly distilled water was obtained from a Millipore Elix 5 water purification system.

2.1 Catalyst preparation and characterisation

For the preparation of the catalysts, the required amount of SWCNT, C or TiO_2 was suspended in double distilled water and stirred vigorously. The necessary volume of 0.02 M $HAuCl_4$ solution required to obtain 5% AuNPs by weight on each support material was added dropwise with continuous stirring. The pH of the solution was maintained at ~8.5 by means of addition of 15% $NaBH_4$ [14]. The precipitated solution was aged under stirring for 2 h. A solution of ice cold 0.02 M $NaBH_4$ was prepared and added as needed to complete the reduction of Au(III) to Au(0) and then the suspended solution was aged while maintaining the pH at 8.5 for a further 2 h. The suspension was then filtered using a 0.45 μm nylon filter and washed with 3 times the suspension volume using doubly distilled H_2O and then the remaining solid mass was dried in an oven for a minimum of 4h at ~120 ºC prior to characterisation.

Three supported gold nanocomposites, gold on titanium dioxide (Au/TiO_2), gold on single walled Au/SWCNT and gold on carbon black (Au/P90) were prepared and systematically characterised using scanning electron microscopy/scanning transmission electron microscopy (SEM/STEM), energy dispersive X-Ray analysis (EDX), X-ray diffraction spectroscopy (XRD), atomic absorption spectroscopy (AAS), (Nitrogen) N_2 adsorption, ultra violet-visible (UV-Vis) absorption spectroscopy and Raman spectroscopy to probe the nanoparticle and support physical