Production and Properties of Commercially Useful Gold Catalysts

Jason S. McPherson and David T. Thompson*
Project AuTEK, Advanced Materials Division, Mintek, Private Bag X3015, Randburg 2125, Republic of South Africa
*DTThompson@aol.com

Introduction

Gold catalysts made in kilogram quantities by Project AuTEK are being used to demonstrate their unique advantages in achieving appropriate activity, selectivity and durability in both liquid- and gas-phase reactions which have commercial potential [1]. The high activity of gold catalysts under mild conditions is a valuable asset in achieving the high selectivities.

We have produced three gold catalyst systems in 15kg batches, with ca 1wt%Au supported on TiO_2, Al_2O_3 and ZnO (AURO*lite*^{TM}) and the methods devised are suitable for further scale-up to 65kg, and this is currently underway. The characteristics and properties of these catalysts will be described. Use of these AuTEK catalysts, and similar gold catalysts of interest, in reactions with high selectivity to give desirable products in chemical processing or pollution control applications will be described.

The selectivity and stability of gold catalysts has been firmly established in the liquid phase, where high activities and yields have been recorded for the oxidation of glucose to gluconic acid. Au has greater activity, selectivity and resistance to deactivation than PGM catalyst systems, and FAL (Germany) has compared the performance of the three AuTEK catalysts with their own long life Au/Al_2O_3 system. The production of glucose this way is also more environmentally friendly and economical compared to the biological (fermentation), chemical, and electrochemical methods. Gluconic acid is a food and beverage additive, used in metals cleaning, and in pharmaceuticals; its worldwide production is 100,000 t/a. The process has been patented by Südzucker Akt [2].

Results and Discussion

In addition to glucose oxidation, AuTEK catalysts have been evaluated in the oxidation of lactose to lactobionic acid [3], aldehydes to esters [4], and citronellal to citronellic acid [5] using oxygen. The complete oxidation of propene and methane to carbon dioxide and water occurs without sintering of the gold nanoparticles. The water-gas shift has also been studied and selective hydrogenation in the gas phase.

$1.9wt\%Au/Al_2O_3$ promotes the continuous gas phase hydrogenation of p-chloronitrobenzene to p-chloroaniline at 393 – 523 K, ΔE_a = 49kJ mol^{-1}. There is no detectable catalyst deactivation over 80 h [6]. $1mol\%Au/TiO_2$ had a higher specific rate than $1mole\%Au/Al_2O_3$ by a factor of up to 4 and both catalysts gave 100% selectivity to the chloroaniline [6]. The AuTEK catalysts have similar activities but are not as durable in this reaction, and the durability surprisingly is produced by comparatively large gold nanoparticles (5 – 9 nm). The gold nanoparticles in AuTEK catalysts do, however, have size-stability during methane oxidation at 250 °C, as shown by gold particle size distribution before and after reaction, by TEM [7].

Gas phase selectivity of gold catalysts has also been confirmed at AuTEK in an unconventional PROX system, designed for the removal of CO from 'dirty' hydrogen. For use in a fuel cell, the carbon monoxide still present in the hydrogen, obtained from this or other sources, must be removed to prevent it poisoning the platinum electro-catalyst inside the fuel cell. $3wt\%Au/TiO_2$ has been shown to be selective for CO at close to ambient temperatures and a space velocity of 850,000 $ml.g_{cat}^{-1}.h^{-1}$. This has enabled Project AuTEK to develop a new system for hydrogen purification for PEM fuel cells, trade named AURO*PureH*$_2^{TM}$ [8,9]. This concept is designed to purify cheap hydrogen on vehicles, with the hydrogen feed for the fuel cell being drawn directly from a cylinder or other on-board storage technologies. Fuel efficiency is essentially maintained and this simple, low cost and practical system allows lower Pt loadings for the fuel cell anode, reducing costs whilst not adding significantly to the weight and volume of the fuel cell system. The AURO*PureH*$_2^{TM}$ system removes carbon monoxide to below 1 ppm (from 10–2000 ppm CO in H_2 with a 1–2 % air bleed, and obviates the need to use PtRu or PtMo anodes in the fuel cell [8]. The gold cost is only ca 2% of the US Department of Energy stipulated target of $45/kW for vehicular fuel cells.

Results of WGS and CO oxidation mechanistic studies on AuTEK catalysts will be reported and discussed, especially with respect to deriving a greater understanding of the mechanisms of these reactions as currently described in the literature [10-12]. A consideration of the relative importance of gold particle size, metal-support interactions, and catalyst pre-treatments will be included.

Significance

Now that gold catalysts are available in commercial quantities, applications are being developed in pollution control, chemical processing and technology for the hydrogen economy. These will take advantage of their activity, durability and selectivity under mild conditions.

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