

A Novel Approach to Catalyst Preparation

Catalysis & Synthesis for Effect is a key priority area identified for action under Chemistry Innovation's strategic plan. The effective application of these technologies can help improve industrial sustainability and profitability, as well as provide new products and materials for the future. Priority Manager - Dr David Parker provides mentoring support to a research team at Cardiff University who are developing 'Novel Approaches to Catalysts Preparation' with funding from an EPSRC Industrial CASE Award.

Heterogeneous catalysis is involved in the manufacture of most finished products from pharmaceuticals to electrical devices. Catalytic processes are inherently green, yielding high atom efficiencies; however, catalyst manufacturing processes have changed little in the last 50 years.

For many mixed oxide or oxide-supported metals, a catalyst precursor is formed by precipitation, hydrothermal synthesis, or grinding and heating; this precursor is then subsequently reprocessed by a heat treatment coupled possibly with a redox step to produce a finished material that can be formed into suitable shapes.

The process is energy intensive, uses large amounts of solvents and produces copious amounts of waste products. A paradox of catalysis, which is perceived to be green when often it is not!

The Cardiff team, led by Professor Graham Hutchings, has developed the use of supercritical CO₂ as the precipitating medium in catalyst manufacture, producing a number of high activity catalysts via this process.

This is exemplified by the following examples:

AMORPHOUS VANADIUM PHOSPHATE (VPO)

The new route using supercritical CO₂ as an anti-solvent, is illustrated for vanadium phosphate (VPO) catalysts below: The amorphous microspheroidal VPO produced was found to be to be 3-4 times more active than comparable crystalline VPO catalysts for the selective oxidation of *n*-butane to maleic anhydride and, furthermore, does not require an extensive pre-treatment or activation period to establish full catalytic activity. This is typically 72 hours for conventionally prepared catalyst.

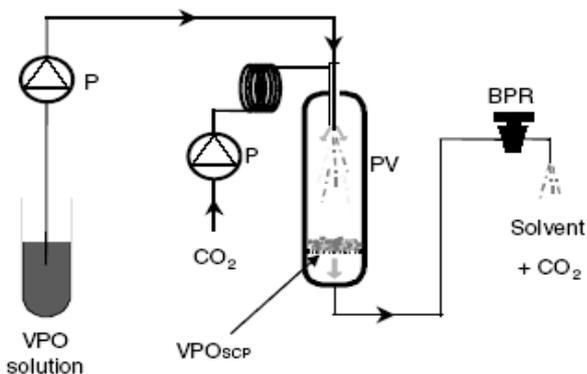
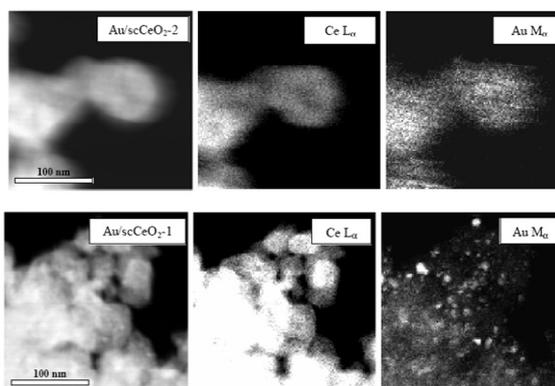


FIG. 1. Schematic of apparatus for the precipitation of vanadium phosphates using either supercritical or liquid CO₂. BPR, back pressure regulator; PV, precipitation vessel; P, pumps.

NANOCRYSTALLINE CERIUM OXIDE (CeO₂)

Nanocrystalline CeO₂ was prepared by precipitation of a solution of the acetate using supercritical CeO₂ as an anti-solvent. It was demonstrated that gold supported on this material is very active for the oxidation of CO at ambient temperature, particularly in comparison with CeO₂ prepared in a conventional manner by thermal decomposition of the acetate. Catalytic activity was found to be ~25 times greater than previous Au/CeO₂ catalysts, due to better dispersion of gold particles.

Most active catalyst has Au well dispersed



Less active catalyst has distinct Au nanocrystals

Fig. 2. Transmission Electron Micrographs of Excellent and Poor Activity Au/CeO₂ Catalysts

A key target for the Cardiff Group is to develop a non-nitrate route for the copper/zinc oxide/alumina methanol catalyst. This is currently prepared by conventional precipitation of soluble nitrate salts with sodium carbonate to yield an insoluble carbonate. It is anticipated that the supercritical CO₂ process will circumvent the need for nitrate salts.

Preparation and use of nitrates contribute greatly to environmental burden and nitrous oxide, a by-product of nitric acid manufacture is >150 times more potent as a greenhouse gas than carbon dioxide. The non-nitrate route is currently the topic of an industrial collaboration with Johnson Matthey Catalysts.

In recognition of their work on more sustainable routes to catalyst manufacture, the research team at Cardiff University were awarded the Envirowise Green Chemistry Award by the IChemE.