Wall coated capillary microreactors with embedded metallic nanoparticles for fine chemicals synthesis

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Introduction

Process intensification in micro-process technology targets the reduction of equipment size by several orders of magnitude to achieve substantial savings in capital cost, improvement of intrinsic safety, reduction of environmental impact, and increase of the yield and selectivity of chemical processes. Within this field, following the realization of the benefits of microfluidic technology over conventional chemical synthesis, chip- and capillary-based microreactor research for fine chemicals synthesis is a rapidly growing area worldwide [1]. Early studies in this field included the preparation of macroporous monolithic capillary microreactors that anchored different catalysts in cross-linked polymer networks, or the use of surface grafting as a means of specifically altering the properties of the porous surface.

Materials and Methods

Pd and PdZn colloidal nanoparticles of approximately 2.5 nm mean diameter were synthesized using a polyol reduction method modified from that described in previous work [2], and the synthesised nanoparticles were dispersed in ethanol. Nanoparticle-doped mesoporous titania thin films (with a 1 wt.% metal loading) were generated following a similar methodology to that published elsewhere [3]. A precursor solution with the following composition was prepared: 1 $Ti(OBu)_4$ (Titanium tetrabutoxide (TTB)); 0.005 Pluronic F127 (BASF Chemical Company); 40 EtOH; 1.3 H_2O; 0.13 HNO_3. The solution was made by adding the appropriate amounts of F127, water, concentrated nitric acid, and TTB to ethanol, in that order.

The solution was used to coat the interior surface of a fused silica capillary with an internal diameter of 250 μm and a length of 10 m. The adhesion was improved by passing a 1 M NaOH aqueous solution. The titania sol was withdrawn from the capillary at a rate of 1 cm/s. The capillary was dried and calcined in an oven at 300ºC at a residual pressure of 15 mbar. Notably, it was found that manipulation of the rate of solution removal from the capillary allowed precise control of the coating thickness on the nanometer scale. A similar coating was deposited on 1x1 cm^2 flat silicon substrates in order to perform characterization.

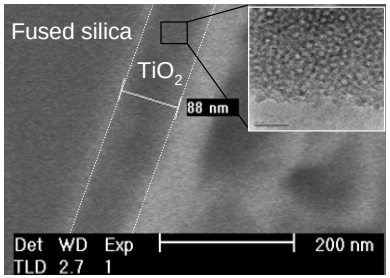

Figure 1. Scanning electron micrograph of the cross-section of the deposited thin film. Inset: TEM showing the ordered mesoporous structure.

The porous structure of the prepared film was determined by ellipsometric porosimetry using the adsorption-desorption of ethanol and by Transmission Electron Microscopy. The hydrogenation of phenylacetylene and 2-methyl-3-butyn-2-ol in the $PdZn/TiO_2$ coated capillary microchannel was studied in the 30-60ºC temperature range.

Results and Discussion

Our experiments indicated that the thin films deposited by dip-coating possessed an ordered porous structure and that the nanoparticles were embedded in their matrix (Figure 1). The reaction rate in terms of TOF for the semihydrogenation of pheylacetylene was found to be up to 2 s^{-1}, a value comparable to that reported for the same Pd nanoparticles in batch reactors. Nanoparticle size and metal ratio can be adjusted very precisely (see Table 1) in order to fit the adsorption mode of specific organic substrates. Furthermore, pore size, porous structure and coating thickness can be modulated to avoid diffusion limitations. Several systems in which these parameters have been varied in order to controllably influence activity and selectivity have been successfully demonstrated. Lastly, the capillary microreactors maintained both their activity and selectivity after more than one month of continuous use under a variety of conditions.

Table 1. Tunable parameters of thin films and selected procedures

Parameter	Procedure
Metallic ratio in the nanoparticle	Change initial precursor concentrations
Nanoparticle size	Change amount of protecting agent (polyvinylpyrrolidine)
Porous structure of the coating	Change surfactant/fractional volume of surfactant in solution
Pore size	Use of co-surfactants (eg. *n*-butanol)
Coating thickness	Change delivery flow rate/Perform multiple depositions

Significance

Herein we have presented the first use of a continuous capillary microreactor with mesoporous thin films incorporated as catalyst supports for multi-phase catalytic reactions. The potential of these novel systems is demonstrated by the results obtained in representative selective hydrogenation reactions of high industrial relevance. The catalytic results indicate that these systems were able to convert a variety of acetylenic alcohols (e.g. 2-methyl-3-butyn-2-ol; dehydrolinalool, dehydroisophytol) into their corresponding semihydrogenated derivatives with high conversions (over 99%) and with selectivities above 95%. This constitutes the first example of catalytic mesoporous thin films used in microreactor technology.

References

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