

Supplementary Information

Capillary microreactors wall-coated with mesoporous titania thin film catalyst supports

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Experimental Section

General preparation of a mesoporous TiO₂ thin film

Following the synthesis solution composition described in the manuscript we proceeded as follows:

- 1) 18.42 g of absolute EtOH was transferred to a polypropylene bottle. 0.64 g of Pluronic F127 (BASF Chemical Company) were added and the mixture was stirred with mild heating (50°C) for 60 seconds. After this time the mixture was completely transparent.
- 2) To this clear solution, 0.19 g of distilled water and 0.13 g of suprapure HNO₃ (65% wt.) were added. Gentle swirling homogenized the resulting solution. A magnetic stirring bar was added and the solution was stirred at a moderate-high rate (approx. 500 rpm.) at room temperature.
- 3) 3.42 g of titanium tetrabutoxide (TTB) were added *dropwise* to the rapidly stirred solution. To do so, the corresponding amount of TTB was pre-weighed in a separate container and then added very slowly to the stirred mother liquor using a pipette.
- 4) After TTB addition, the resulting mixture was stirred at room temperature for 2 hours in order to age the solution. The resulting clear solution was then transferred to a glove box in order to perform the dip-coating and spin-coating procedures.

Preparation of a mesoporous TiO₂ thin film with confined nanoparticles

The procedure was as above, except that a fraction of the absolute EtOH was substituted by a given amount of colloidal suspension (in absolute EtOH). As an example, when synthesizing a Pd-doped thin film, a colloidal suspension which contained 0.6 mg of Pd/ml of solvent was used. Thus, considering the amount of TTB used in the previous example, upon complete hydrolysis it would produce 802.6 mg of pure TiO₂. To obtain a 1%wt. loading of Pd in the resulting thin film 8.03 (subscript?) mg of Pd nanoparticles are needed. Given the concentration of the suspension, 13.38 mL (10.59 g, assuming that the

density of the absolute EtOH is not significantly changed by the presence of the nanoparticles) of the colloidal suspension are required. Thus in the first step of the previous protocol 10.59 g of the colloidal suspension and 7.83 g of absolute EtOH are needed, leaving the rest of the synthetic protocol unchanged.

Preparation of a mesoporous thin film with large pore size

Mesoporous thin films with a pore size of 5 nm were prepared by dissolving surfactant in ethanol, after which $\text{Ti}(\text{OiPr})_4$ precursor was added and the pH adjusted to 1.5 by the addition of concentrated nitric acid. The resulting solution, which had the molar composition 1 $\text{Ti}(\text{O}-i\text{C}_3\text{H}_7)_4$; 0.009 Pluronic F127; 40 ethanol; 1.3 H_2O ; 0.13 HNO_3 , was stirred at r.t. for 2 hours. Delivery of thin films was performed by spin-coating on flat silicon substrates. An aliquot (50 μL) of the solution sol was placed on the support and spin-coating was performed for 30 seconds at 1500 rpm with an acceleration rate of 1250 rpm/s. The plates were left in the glove box for 24 hours at a RH of 80% and then calcined at 300°C under a residual pressure of 10 mbar with a heating rate of 1°C/min to remove the surfactant.

Figure 1 shows the ethanol adsorption isotherm obtained at 14°C. The shape of the isotherm is very similar to that presented in the manuscript, with the exception that both the adsorption and desorption branches are shifted towards higher relative pressure values, indicating a more open porous structure. The pore size distribution plot obtained from the desorption branch of the isotherm shows that the pore size is approximately 5 nm.

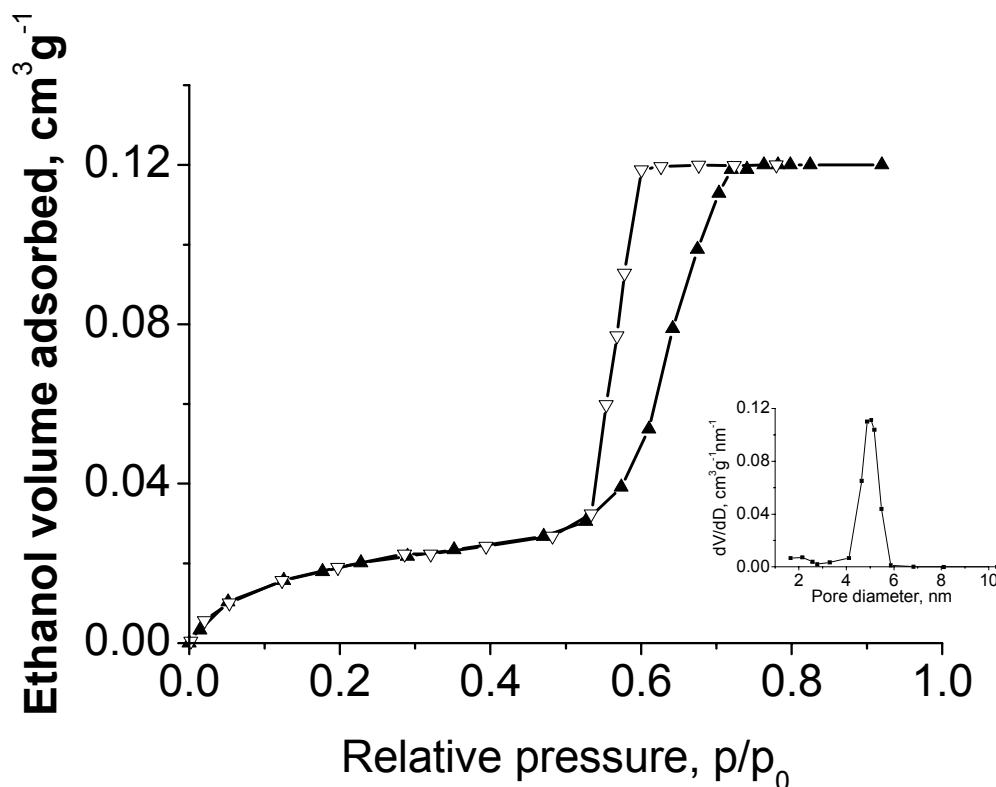


Figure 1. Ethanol adsorption-desorption isotherm obtained of a large-pore TiO₂ thin film deposited on a silicon wafer

As indicated in the manuscript, by altering the protocol of the thin film synthesis, we are able to tune the pore size of the resulting mesoporous solid to provide the coating with greater accessibility for larger nanoparticles, or to avoid diffusion limitations, thus demonstrating the versatility of the systems described in this study (see manuscript).

Confinement of a bimetallic colloid in a mesoporous TiO₂ thin film

In order to test the feasibility of incorporating bimetallic systems within the structure of a synthesized TiO₂ thin film, the synthetic protocol described in the manuscript was repeated using bimetallic Pt:Ru (20:80) colloids. Figure 2 shows the electron micrographs obtained for this sample.

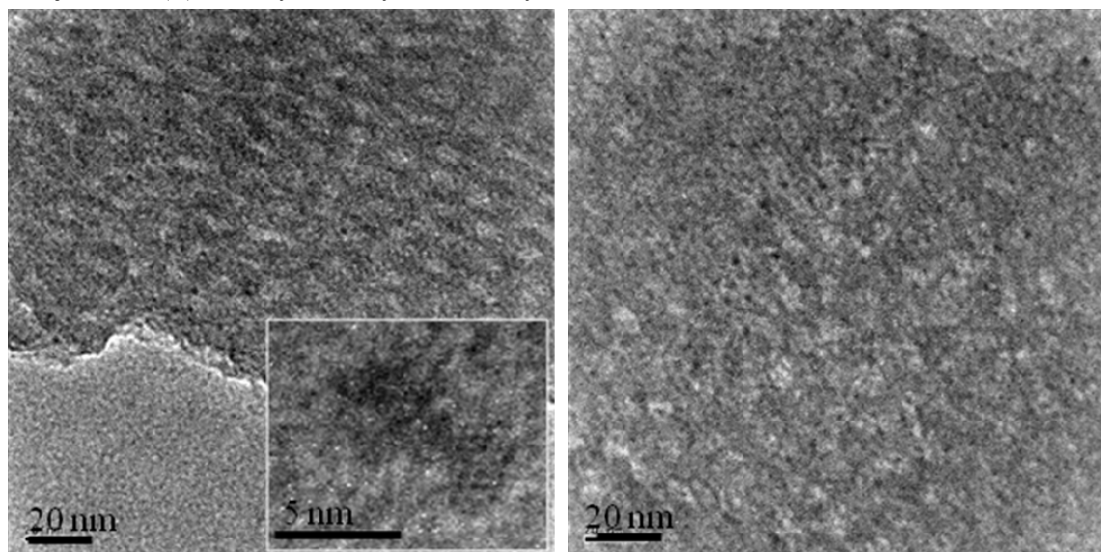


Figure 2. Left: TEM showing the mesostructural ordering of a TiO₂ thin film incorporating 1 wt.% of confined Pt:Ru (20:80) nanoparticles. Inset: HR-TEM picture showing two independent confined nanoparticles. Right: Transmission Electron Micrograph of the same thin film under a different focus showing several nanoparticles (black dots).

Characterisation

Low-angle X-ray diffraction spectra were recorded on a Rigaku Geigerflex device with Cu K α radiation (40kV, 40 mA), 0.01-0.02° step size, with a counting time of 4.0 s. High-resolution Transmission Electron Microscopy studies were performed using a JEOL JEM-3011 electron microscope operating at 300 kV with a structural resolution of 0.16 nm. The samples were prepared by scratching off the silicon wafer-deposited films with a clean scalpel blade, using a droplet of demineralised water as suspending fluid. A drop of the suspension was deposited on a carbon-coated copper grid, followed by drying under ambient conditions.

Catalytic Testing

A mixture of 10 vol.% phenylacetylene in methanol and hydrogen was generated by employing a T-mixer prior to the microchannel. The temperature, gas and liquid flow conditions were carefully selected in order to work under ring flow conditions [1]. The liquid flow was varied between 1 and 10 μ L/min and the hydrogen flow between 250 and 550 μ L/min (STP), corresponding to superficial velocities of 0.034-0.34 cm/s and 8-18 cm/s for liquid and gas, respectively. The gas and liquid were mixed in a T-mixer, the internal diameters of the inlet and outlet tubes of which measured 250 μ m. The gas was fed at an angle of 90° with respect to the liquid flow. In the range of gas and liquid velocities applied, an annular two-phase flow was realized in the microchannel, such that the gas flowed along the centre of the tube, while the liquid flowed along the channel walls as a liquid film. The thickness of this liquid film determined the resistance to

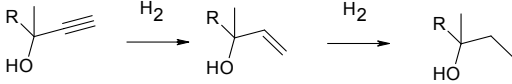
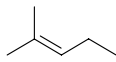
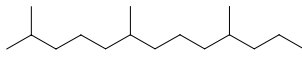
transfer of the gas from the gas core through the film to the catalyst. This resistance decreased with increasing gas flow rate and increased with increasing liquid flow rate.

The liquid samples containing the reaction products were collected at the outlet of the capillary, diluted (1:10) in methanol and analyzed on a Varian CP-3800 gas chromatograph equipped with a CP-Sil 5CB capillary column (operating at 85°C) and a FID detector.

Effect of metal ratio of colloidal nanoparticles on catalytic performance

The adsorption mode of homologues of terminal acetylene alcohols (see Table 1) viz, Dimethylethynylcarbinol (DMEC, 2-methyl-3-butyne-2-ol, C₅H₈O) ; Dehydrolinalool (DHLN 3,7-dimethyl-6-octaen-1-yne-3-ol, C₁₀H₁₆O); and Dehydroisophytol (DHIP, 3,7,11,15-tetramethyl-1-hexadecyne-3-ol, C₂₀H₃₈O), can be significantly influenced by the use of different metallic ratios in the catalytic nanoparticles. Figure 3 shows the difference in selectivities obtained in the hydrogenation reaction of DMEC, DHLN and DHIP using different Pd/Zn nanoparticles in a batch reactor.

Table 1. Reactants, target products and side products of industrially relevant hydrogenations of acetylene alcohols.

			
R	Reactant	Target product	Side product
H ₃ C-	Dimethylethynylcarbinol (DMEC) C ₅ H ₈ O 2-methyl-3-butyne-2-ol	Dimethylvinylcarbinol (DMVC) C ₅ H ₁₀ O 2-methyl-3-buten-2-ol	Dimethylethylcarbinol (DiMEC) C ₅ H ₁₂ O 2-methylbutan-2-ol
	Dehydrolinalool (DHLN) C ₁₀ H ₁₆ O 3,7-dimethyl-6-octaen-1-yne-3-ol	Linalool (LN) C ₁₀ H ₁₈ O 3,7-dimethyl-1,6-octadiene-3-ol	Dihydrolinalool (DiHNL) C ₁₀ H ₂₀ O 3,7-dimethyl-6-octaen-3-ol
	Dehydroisophytol (DHIP) C ₂₀ H ₃₈ O, 3,7,11,15-tetramethyl-1-hexadecyne-3-ol	Isophytol, (IP) C ₂₀ H ₄₀ O, 3,7,11,15-tetramethyl-1-hexadecene-3-ol	Dihydroisophytol (DiHIP) C ₂₀ H ₄₂ O 3,7,11,15-tetramethyl-hexadecane-3-ol

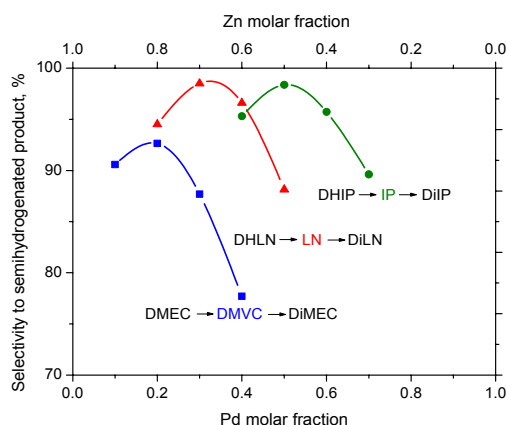


Figure 3. Selectivity of supported PdZn/C catalyst in selective hydrogenation of terminal acetylene alcohols obtained at a conversion of 99% at 60 °C in a batch reactor.

Depending on the length of the organic fragment, different Pd/Zn ratios in bimetallic catalysts are required to obtain the maximum yield. Large organic fragment in the substrate molecule, can stronger polarize the C-C triple bond, so less electropositive metal is required in the bimetallic colloid. Increasing electron density on Pd leads also to decreasing interaction with electron-rich compounds. In so doing, the decreased alkene adsorption would favor its desorption and increased selectivity.

References

- [1] V. Haverkamp, V. Hessel, H. Löwe, G. Menges, M.J.F. Warnier, E.V. Rebrov, M.H.J.M. de Croon, J.C. Schouten, M. Liauw, *Chem. Eng. Technol.*, 2006, **29**(9), 1015