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Additional Information

POROUS CATALYSTS

Separate to accumulate

A sequential templating technique yields bifunctional catalysts with controlled separation of cooperative catalytic functionalities.

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The design of solid catalysts with well-defined active sites has become commonplace thanks to the ease by which structured micro- and mesoporous materials (such as inorganic zeolites, as well as organic and hybrid frameworks) can be controllably modified with small catalytic groups. It is also quite feasible to synthesize structured catalysts that are able to perform multiple reactions by incorporating different catalytic groups within the same framework support, thus avoiding the need for additional and costly synthesis and purification steps^{1–3}. Furthermore, by coupling these separate catalytic activities it is possible to carry out sequential chemical reactions; indeed, bifunctional supports bearing both acidic and metal catalysts have been used in this way to enhance a range of important industrial processes, such as the catalytic reforming of hydrocarbons, alkane hydroisomerization and hydrocracking^{4,5}. Typically, the close proximity of the two types of active site in these systems is an important requirement to achieve optimal efficiency of stepwise reactions⁶. However, it is also conceivable that certain multistep processes could benefit from the separation of individual catalytic groups to different environments within the same material, though this obviously raises questions on how the link between the component reactions can be maintained. A group of researchers led by Adam Lee at the University of Aston now present a new catalyst design for the spatial isolation of individual catalytic metals within connected macro- and mesoporous networks of a hierarchical porous silica support, enabling multistep catalytic reactions⁷.

The synthetic methodology which the authors developed to make their so-called spatially orthogonal bifunctional porous catalyst (as illustrated in Fig. 1) is quite ingenious. They used lyotropic liquid crystal templating to synthesize a hierarchically ordered macro-mesoporous silica (SBA-15). This was achieved by forming mesoporous silica using a pluronic surfactant (P123) template, around an ordered array of polystyrene colloidal nanospheres. They

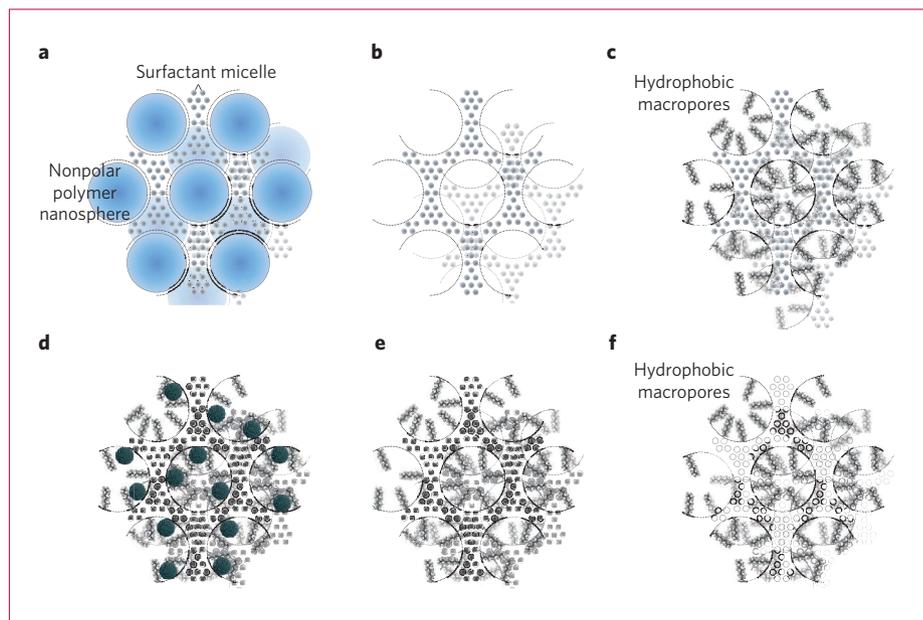


Figure 1 | Illustrated synthetic strategy for spatially orthogonal functionalization of hierarchical architectures. **a, b**, Parent polystyrene colloidal nanospheres encapsulated within a P123-templated SBA-15 silica network (**a**), and the ordered macroporous framework after selective removal of the polystyrene macropore template (**b**). **c**, Selective hydrophobization of the macropore framework by triethoxyoctylsilane. **d**, Ordered hydrophobized macropores and ordered mesopores following P123 extraction. **e**, Mesopore channels selectively functionalized with Pt nanoparticles [Au: OK?]. **f**, Hydrophobic macropores selectively functionalized with oleylamine-stabilized Pd nanoparticles. [Au:OK?] Image reproduced from ref. 7, Nature Publishing Group.

then carried out independent extractions of the templates such that they could selectively functionalize the internal pore networks with the catalytic metals Pd and Pt. They firstly removed the macropore template (polystyrene) and attached octyl groups to promote hydrophobization. They then removed the mesopore template (P123), and due to the engineered hydrophobicity of the macropores, they were able to selectively impregnate the mesopores with nanoparticulate Pt using an aqueous solution of H_2PtCl_6 . For the second functionality, they use oleylamine-capped colloidal Pd nanoparticles which, at ~5.6 nm diameter, were spatially limited to functionalize only the macropores. Importantly for catalytic applications, the

metals did not block the pores, and the surface area and pore volume distribution were maintained after the extraction-impregnation-activation treatments.

To demonstrate the catalytic benefit of the spatially orthogonal chemical functionalization within their hierarchical pore network, the authors performed a stepwise oxidation of cinnamyl alcohol, via cinnamaldehyde, to cinnamic acid (Fig. 2a). The alcohol reactant first encountered the Pd-functionalized macroporous network in the initial reaction, and the aldehyde formed then diffused throughout the Pt-modified mesopores where the second catalytic reaction took place, to give the final acid product. These reactions individually are very well known. Pd has been used

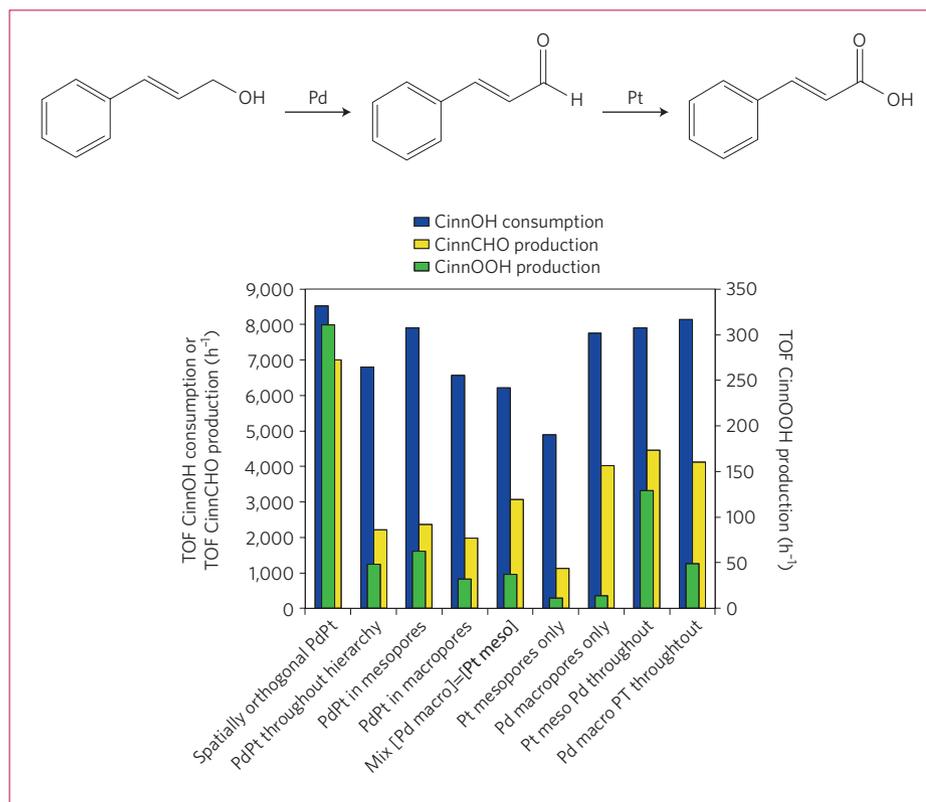


Figure 2 | The catalytic cascade. **a**, The chemical pathway of cinnamyl alcohol oxidation to cinnamic acid via cinnamaldehyde. **b**, Reaction dynamics of cinnamyl alcohol oxidation. Active site-normalized rates of cinnamyl alcohol conversion (blue), and cinnamaldehyde (yellow) and cinnamic acid (green) production for the one-pot cascade oxidation of cinnamyl alcohol over the hierarchical Pd macroporous-Pt mesoporous SBA-15 catalyst (1 wt% in each metal), and a range of bimetallic and monometallic SBA-15 analogues. Panel **b** reproduced from ref. 7, Nature Publishing Group.

previously as a catalyst for cinnamyl alcohol oxidation to give the corresponding aldehyde, while Pt is a known catalyst for the oxidation of cinnamaldehyde to give cinnamic acid. However, Pd is also quite able to decarbonylate [Au: decarboxylate?]

the aldehyde intermediate, while Pt readily reacts with the alcohol starting material. By spatially isolating the catalytic metals within their new framework, the authors were able to promote the desired cascade reaction whilst minimizing any opportunity for the

metals to participate in competing side reactions. This represents the first one-pot system able to carry out this process using a single heterogeneous catalyst. Figure 2b shows the catalytic results obtained with different Pd-Pt arrays within the pores, and it is clear that the maximum turnover frequencies for aldehyde and acid formation were achieved when Pd was located at the macropores and Pt in mesopores.

Despite this impressive proof-of-concept, the work falls somewhat short of demonstrating a catalytic process with real practical value; an improved overall conversion efficiency from the alcohol to the acid would be required to claim this. Also, a more suitable catalytic cascade would be one in which the controlling step of the reaction is the diffusion of the first reactant through the macropores. Nevertheless, as a first step, this work details a particularly interesting methodology for preparing spatially orthogonal functionalized hierarchical porous networks, and by achieving a higher overall conversion of the intermediate, the full potential of these bifunctional catalysts for use in promoting cascade chemical reactions will be realised. □

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