

Solid Nanoparticles that Catalyze Biofuel Upgrade Reactions at the Water/Oil Interface

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A recoverable catalyst that simultaneously stabilizes emulsions would be highly advantageous in streamlining processes such as biomass refining, in which the immiscibility and thermal instability of crude products greatly complicates purification procedures. Here, we report a family of solid catalysts that can stabilize water-oil emulsions and catalyze reactions at the liquid/liquid interface. By depositing palladium onto carbon nanotube–inorganic oxide hybrid nanoparticles, we demonstrate biphasic hydrodeoxygenation and condensation catalysis in three substrate classes of interest in biomass refining. Microscopic characterization of the emulsions supports localization of the hybrid particles at the interface.

In phase-transfer catalysis, reactions are carried out in a biphasic mixture of two immiscible solvents, often water and a hydrophobic organic liquid; added surfactants such as quaternary ammonium salts enhance interfacial surface area (through emulsification) and facilitate transfers between the phases (*1*). The technique is especially useful in cases in which a product might otherwise be unstable under the reaction conditions in one phase but can partition into the other phase after rapid formation. More broadly, ongoing partitioning of by-products on the basis of their relative solubility can result in substantial simplifications at the isolation and purification stages, obviating the need for procedures such as distillation that might damage heat-sensitive compounds. Such process improvements could have a major impact in the field of biomass conversion to fuels. For example, bio-oil obtained from pyrolysis of biomass is a complex liquid that is only partially soluble in either water or hydrocarbon solvents (*2*). Rather than carrying out multiple consecutive purification steps during refining to separate out the hydrophilic by-products incompatible with fuel applications (*3*), it would be desirable to perform sequential reactions under phase-transfer conditions in a single reactor medium.

A serious drawback in such systems, however, is that the surfactants can be difficult to separate from final product mixtures. Solid particles are more easily recoverable and have also been shown in many cases to stabilize aqueous-organic emulsions (*4–7*), but these solid-stabilized emulsions have not been widely used in catalytic contexts. Moreover, in cases such as the refining of bio-oils in which the system is biphasic and contains up to 30% water, the most efficient way of catalyzing reactions is to place the solid catalyst at the liquid/liquid interface and to maximize the extent of interface by creating an emulsion. Otherwise,

the catalyst particles will preferentially remain in the heavier phase, such as water. In that case, only the water-soluble molecules will be converted. If further conversion of water-insoluble molecules is wanted, one would need to remove them from the top of the reactor and send them to another reactor with a catalyst operating in the organic phase. Therefore, the concept of solid particles that can simultaneously stabilize an emulsion and catalyze reactions in both phases becomes an attractive proposition.

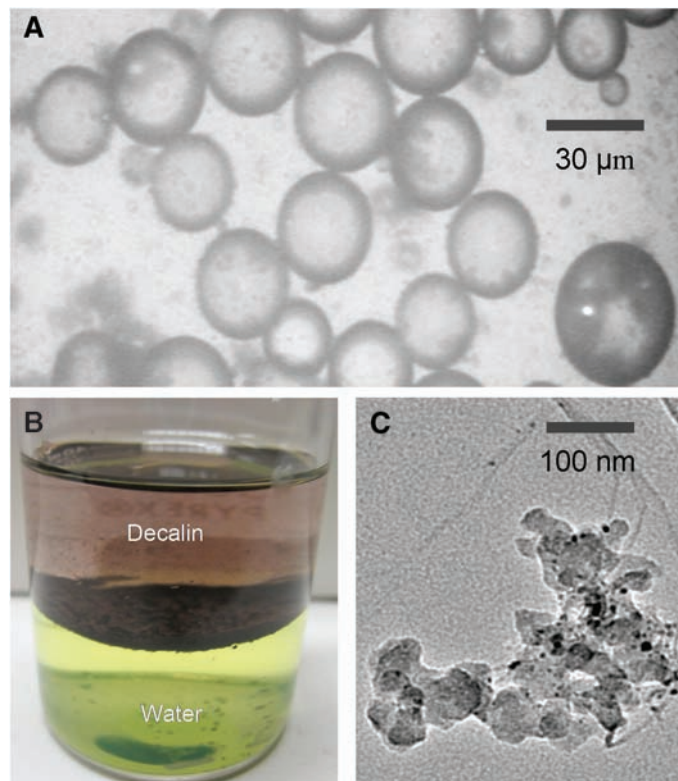
In particular, oxide nanoparticles have previously been used to stabilize oil-in-water emulsions (*8–10*) because their hydrophilicity preferentially orients them toward the aqueous phase at the inter-

face. Carbon nanotubes have also been shown to produce emulsions, but of the water-in-oil variety because they are hydrophobic (*11*). We recently prepared hybrid nanoparticles by fusing carbon nanotubes to silica (*12*). By tuning their composition, we could modify the hydrophilic-hydrophobic balance and assemble water-in-oil or oil-in-water emulsions systematically and reproducibly (*13*). The emulsion volume fraction in the three-layer system formed (oil-emulsion-water) and the droplet size were greatly influenced by the oil-to-water ratio in the mixture and the degree of oxidative functionalization of the nanotubes. In this contribution, we have undertaken a more detailed characterization of the structure of these emulsions using optical and electron microscopy [figs. S14 to S16 and supporting online material (SOM) text] (*14*).

One of the main objectives of the present study was to extend the utility of these nanohybrids by incorporating a transition metal, rendering them catalytically active for hydrogenation. The second objective was to add a solid base function to catalyze condensation reactions.

As shown in Fig. 1, after the addition of Pd metal particles these particles still straddle the organic/aqueous interface, and the appearance and stability of the emulsions formed are unaffected. We envisioned that their selective metal functionalization would be a powerful strategy for directing reactivity in a specific phase: Depositing a metal such as Pd on the hydrophilic face would catalyze aqueous reactions, whereas deposition on the hydrophobic face would favor chemistry in the organic solvent. In fact, established catalyst

Fig. 1. (A) Optical microscopy image of a water-in-oil emulsion formed by sonicating a 1:1 mixture of decalin and water in the presence of 5 weight percent (wt %) Pd/SWNT-SiO₂ nanohybrids. (B) The same mixture as in (A) before sonication. It is seen that the nanohybrids preferentially migrate to the interface. (C) TEM image of the 5 wt % Pd/SWNT-SiO₂ nanohybrids. It is apparent that Pd clusters are preferentially located over the silica surface rather than over the nanotubes.



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preparation methods exist that can be used to selectively deposit metal precursors from solution on either silica or nanotubes, depending on the pH of the solution and the point of zero charge of the substrate (15–17).

In this work, we have explored two preparations with nanotubes of different type. This difference affects the deposition of Pd. As shown in Fig. 1C, in the first preparation the incipient wetness impregnation method used to deposit Pd on the single-walled carbon nanotube (SWNT)–silica nanohybrids results in preferential deposition onto the silica side. This preferential deposition is

due to the very low density of defects on the SWNT walls, as demonstrated by means of transmission electron microscopy (TEM) and Raman spectroscopy (fig. S1). Without defects, the SWNT cannot effectively anchor the Pd nanoparticles, which during the heat treatments end up on the silica surface. In contrast, on the second preparation type, which involves MgO as a support instead of SiO₂, the resulting nanotubes are more defective than those in the first preparation, as also shown by means of TEM and Raman spectroscopy (fig. S2). Consequently, they are more effective in retaining Pd particles. Therefore, we

have been able to demonstrate different degrees of hydrogenation activity in the organic phase by simply using different formulations of the nanohybrids.

We present here the results obtained for several reactions of relevance to biomass-refining chemistry. Two of the major goals in the refining of liquids derived from lignocellulosic sources are the elimination of oxygen and the condensation of small molecules. The former is needed to improve the low stability caused by the high reactivity of the oxygenated functional groups in molecules such as the phenolic compounds de-

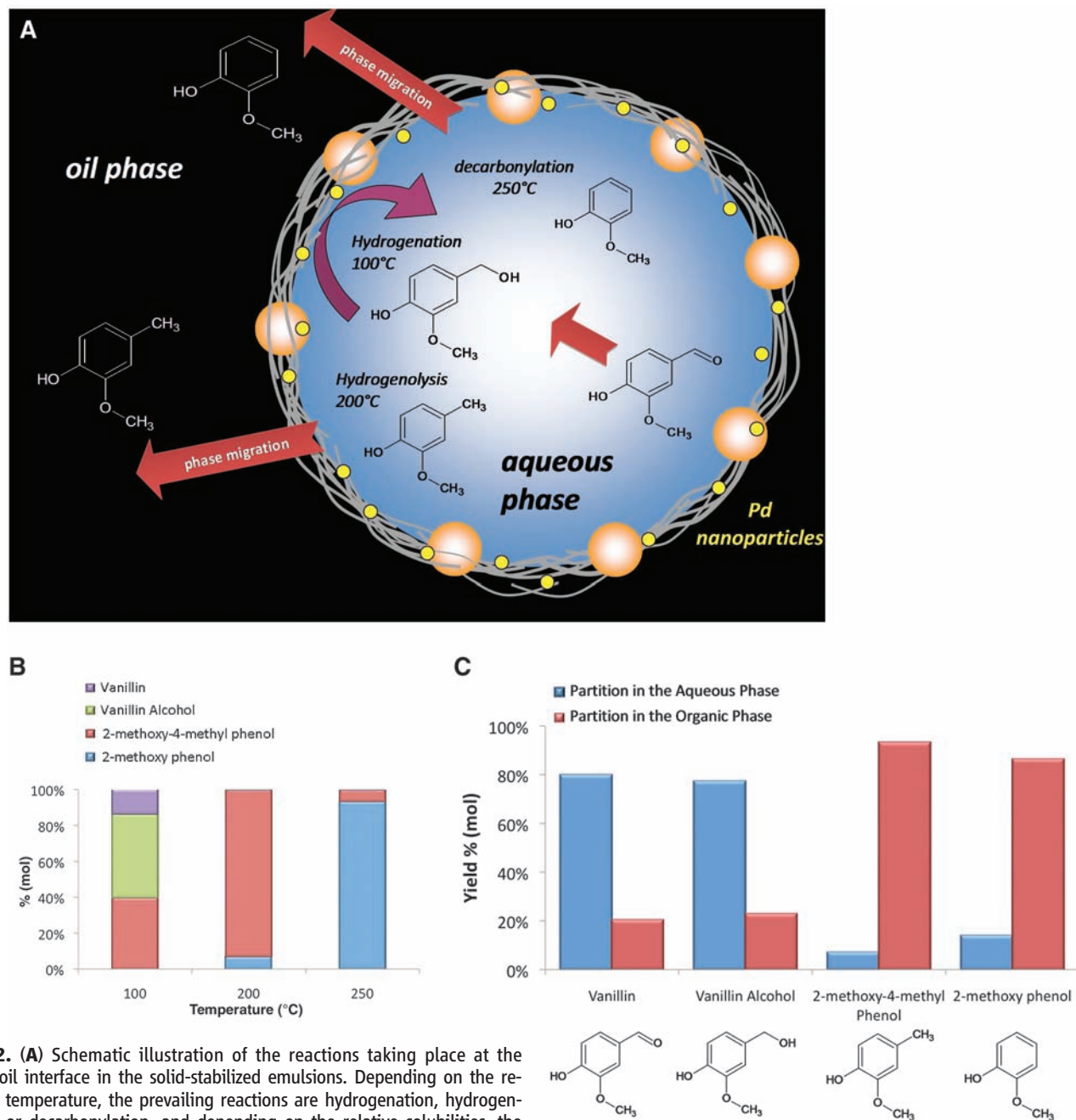


Fig. 2. (A) Schematic illustration of the reactions taking place at the water/oil interface in the solid-stabilized emulsions. Depending on the reaction temperature, the prevailing reactions are hydrogenation, hydrogenolysis, or decarbonylation, and depending on the relative solubilities, the products remain in the aqueous phase or migrate to the oil phase. (B) Total weight fraction of the various products as a function of temperature after 30-min reaction in a batch reactor, from gas chromatographic analysis of each phase (combined). (C) Partition of the various products as in (B) between the individual aqueous and organic phases.

rived from lignin (18, 19). The latter is particularly important to increase the molecular weight of those light fragments derived from the less refractory parts of the biomass (cellulose and hemicellulose).

To illustrate the application of the catalytic nano-hybrids in emulsions, we chose the hydrodeoxygenation of a phenolic compound and the hydrogenation and etherification of an aldehyde on Pd as model reactions that occur in the aqueous side of the interface. Therefore, we have used the nano-hybrids that preferentially have Pd on the hydrophilic side.

In addition, we have been able to replace silica as the hydrophilic component in the nano-hybrids with a basic oxide, magnesia, which not only is effective in stabilizing emulsions but also provides catalytic activity for base-catalyzed reactions, such as the Aldol condensation. In this case, as mentioned above, the hydrophobic side contains nanotubes that are more defective, which allow stabilization of Pd. Therefore, hydrogenation on the oil side is readily observed.

To explore the catalytic application of Pd-containing nano-hybrids to phenolic hydrodeoxygenation in a water-in-decalin emulsion, we chose vanillin (4-hydroxy-3-methoxybenzaldehyde) as a test substrate because it is a common component of pyrolysis oil derived from the lignin fraction (20, 21). This compound was appealing for study because of its three different types of oxygenated functional groups (aldehyde, ether, and hydroxyl) and its partial solubility in both the organic and aqueous phases.

The reaction was carried out in a batch reactor at three different temperatures (100, 200, and 250°C) for different reaction periods. In each run, the molar ratio of vanillin to Pd in the reactor was about 100. After each reaction period, the emulsion was broken by filtering out the nano-hybrid particles. The filtering was conducted in two steps. In the first one, a common paper filter was used. This coarse filter (8- μm pores) was able to trap a large fraction of nano-hybrids because they quickly agglomerate when they contact the filter. In the second step, a polytetrafluoroethylene (0.2- μm pores) filter was used to separate the small fraction of nano-hybrids that passed the first filter. The two liquid phases were separated and analyzed individually by means of gas chromatography with flame ionization (FID) and mass spectrometry (MS) detectors. It was then possible to monitor the migration that the different products underwent from the aqueous to the organic phase, as summarized in Fig. 2. Whereas vanillin and vanillin alcohol were highly soluble in the aqueous phase, the products resulting from both hydrogenolysis and decarbonylation were much more soluble in the decalin phase. As a result, the water-insoluble compounds, which are more valuable as fuel components, can be readily incorporated in the product stream.

The turnover number measured at the lowest temperature tested (100°C) was about 0.2 s^{-1} , which is of similar magnitude to that observed by

others in the hydrogenation of guaiacol catalyzed by Pd/C in a monophasic system but at higher temperatures (150°C) (19). The higher activity observed in the biphasic system could be ascribed to (i) a better state of particle dispersion at the interface as compared with that in the monophasic system (fig. S13) and/or (ii) enhanced hydrogen concentration at the interface (hydrogen has higher solubility in organic phase than in water).

As illustrated schematically in Fig. 2A, we observed a range of different products and phase-migration processes that were due to the varying extents of hydrogenation, hydrogenolysis, and decarbonylation reactions catalyzed by Pd as the reaction conditions were modified. As shown in Fig. 2B, the chemoselectivity changes significantly with increasing temperature. At 100°C, initially only hydrogenation of the aldehyde to the vanillin alcohol is observed, whereas at longer reaction times the alcohol is further converted into 2-methoxy-4-methylphenol (p-cresol) via hydrogenolysis. At 200°C, hydrogenolysis becomes the dominant path even at short reaction times. At 250°C, the dominant reaction is the decarbonylation of the aldehyde group, leading primarily to o-methoxyphenol (guaiacol).

The variation of product distribution with reaction time in the batch reactor at 100°C is shown in fig. S5. The vanillin alcohol is the primary product, but at longer times it is consumed by hydrogenolysis to form p-cresol, which migrates to the organic phase upon formation, preventing further conversion. In contrast, the alcohol remains in the aqueous phase and continues reacting. This result illustrates the concept of simultaneous reaction and separation of intermediate products.

We next explored the reactivity of molecules that were exclusively soluble in either the organic or aqueous phase. Octanal and glutaraldehyde were chosen as the model compounds soluble in

the decalin and water phases, respectively. Three reaction runs were compared at the same conditions (14). In one of them, octanal and glutaraldehyde were partitioned in an equimolar mixture of water and decalin. In the other two, octanal and glutaraldehyde were separately dissolved in pure decalin and pure water, respectively. These molecules were readily hydrogenated over Pd to the corresponding alcohols. However, the nano-hybrids that were used in this case had the metal preferentially deposited on the hydrophilic side. Therefore, we anticipated to see a greater effect on the conversion of glutaraldehyde. Indeed, although only 58% conversion was obtained in the single aqueous phase after 3 hours at 100°C, practically all (98%) of the glutaraldehyde was converted in the emulsion under the same conditions. This enhancement can be ascribed to a combination of selective deposition of Pd on the polar silica as well as the increased exposure of the catalyst at the interface, as compared with the highly aggregated state of the solid catalyst suspended in the one-phase system. Although 5-hydroxypentanal was the expected primary product from the initial hydrogenation of one of the carbonyl groups in glutaraldehyde, this product was not observed. Instead, the cyclic hemiacetal, valerolactol, emerged as a major product. We suspect that the cyclization of the hydroxylaldehyde occurs via attack by the nucleophilic oxygen of the alcohol at the carbonyl carbon, which is analogous to the well-known cyclization of glucose (22).

The time evolution of the products (fig. S6) indicates that the reaction sequence is glutaraldehyde \rightarrow δ -valerolactol \rightarrow 1,5-pentanediol, with the diol dominating at long reaction times. An additional product, 5-hydroxy-1-pentyl tetrahydropyranyl ether, was also observed, but in low yield (<2%). Whereas glutaraldehyde, octa-

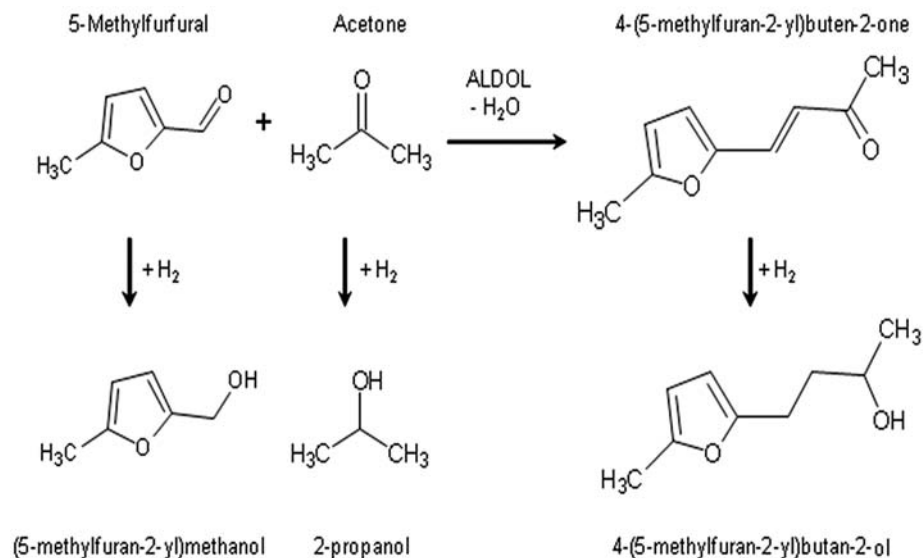


Fig. 3. Possible reaction paths and products arising from the condensation and direct hydrogenation of 5-methylfurfural and acetone over 5 wt % Pd/CNT/MgO.

nediol, and valerolactol remained in the aqueous phase, the ether migrated to the decalin phase. This is an example that illustrates the potential of the method by which one can easily separate an intermediate product from the reaction mixture—even when it is obtained at low yield—before it continues reacting.

At higher temperature, the ether underwent decarbonylation or hydrogenolysis before leaving the aqueous phase, producing 2-butoxytetrahydro-2H-pyran or 2-pentyloxytetrahydro-2H-pyran, respectively. In good agreement with the very high log *P* values of these two products, they were observed exclusively in the oil phase, once again demonstrating the concept of separation after reaction. This result shows that one could arbitrarily modify selectivity by controlling the relative rates of reaction and migration out of the phase in which the catalyst is located. Analogous to shape-selectivity in zeolites (23) and selectivity affected by mass transfer phenomena (24), we can introduce the concept of a phase-transfer selectivity, by which the product distribution resulting from reactions catalyzed at the liquid/liquid interface is modified by the transport to and through the interface, where the catalyst resides. One could design emulsion systems with varying character-

istics (such as droplet size, emulsion type, and relative solubilities) that may affect the residence time of intermediate products in one phase before it migrates to the other phase. This controlled migration may in turn affect the extent of reaction of one specific intermediate.

Because very little Pd was present on the hydrophobic side, in the case of the octanal reaction we observed the opposing result: an activity enhancement in the pure organic phase relative to the emulsion. The octanol yield on the single phase was 9.1%, whereas that in the emulsion was only 2.3%. We ascribe this outcome to the larger proportion of Pd deposited on the hydrophilic oxide than on the hydrophobic nanotubes, as shown in Fig. 1C by means of TEM. The direct hydrogenation of octanal in the organic phase yielded 1-octanol as the (expected) dominant product, together with a small quantity of the symmetric dioctyl ether derived from alcohol coupling.



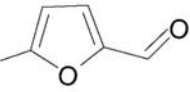
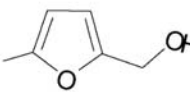
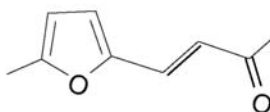
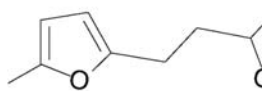
Finally, we explored a tandem reaction sequence in which Pd-catalyzed hydrogenation was paired with a preceding Aldol condensation of 5-methylfurfural and acetone. This reaction was catalyzed by MgO, which was incorporated in the nanohybrids instead of silica. When using

MgO during the nanotube synthesis, the SWNT product contains about 20% multiwalled carbon nanotubes (MWNTs) as an impurity; however, the use of MgO imparts basicity to the nanohybrids, which is crucial for the Aldol condensation. Therefore, because the MgO-based nanohybrids are still effective in stabilizing emulsions, we have been able to conduct reactions at the liquid/liquid interface by using a bifunctional catalyst that contains both metal and basic sites. Moreover, as mentioned above, this nanohybrid contains nanotubes that are more defective and is able to stabilize Pd particles not only on the hydrophilic side but also on the hydrophobic side. Therefore, hydrogenation can occur on both sides of the emulsion.

As represented in Fig. 3, the expected products from the combination of these reactions are 4-(5-methylfuran-2-yl)buten-2-one, 4-(5-methylfuran-2-yl)buten-2-ol, 5-methylfuran-2-yl methanol, and 2-propanol. To better determine how these products evolve, we conducted this reaction in tandem. That is, we first ran the reaction under N₂ at 80°C for 3 hours and analyzed the products, which is indicated as reaction 1 in Table 1. In this case, no hydrogenation took place. Self-condensation of acetone was not observed. Ketone-ketone condensation reactions are thermodynamically less favorable and much slower than ketone-aldehyde condensation, as pointed out by West *et al.* (25). As a result, the major product was 4-(5-methylfuran-2-yl)buten-2-one, which in line with its high log *P* value (~1.5) migrated almost completely to the organic phase. In the second experiment, which is indicated as reaction 2 in Table 1, an additional 1-hour reaction step at 100°C under H₂ flow was added to the initial 3 hours at 80°C under N₂. The 4-(5-methylfuran-2-yl)buten-2-one is totally hydrogenated in the second step, indicating that hydrogenation has occurred in the organic phase as well as in the aqueous phase.

The shorter oxygenates, in this case propanol, remain in the aqueous phase, thus enhancing the probability of realizing further condensation reactions that would be advantageous in the production of fuel components. Similar reactions have been previously described by Dumesic and co-workers (26, 27), operating with a monophasic system. The advantage of operating in a biphasic system, with the catalyst at the liquid/liquid interface, is the possibility of conducting the sequential reactions in a single reactor instead of two. The carbon chains migrate to the organic phase after growing long enough to become hydrophobic, facilitating their isolation as desirable products, whereas the shorter chains remained in the aqueous phase to undergo further growth. The use of a biphasic system provides the possibility of doing the next reaction (for example, hydrogenation-hydrogenolysis exclusively in the oil phase) but in the same reactor. In previous studies conducted in a monophasic aqueous system (26), once the water solubility of the condensed product becomes low enough, it leaves this phase, stopping the conversion. In many cases, these intermediate products

Table 1. Product distribution of the Aldol-condensation–hydrogenation reaction of 5-methylfurfural and acetone over 5 wt% Pd/(CNT/MgO). Reaction conditions were 3 hours at 80°C in 250 pounds per square inch (psi) of N₂ and then 1 hour at 100°C in 250 psi of H₂. Aq., aqueous phase; Org., organic phase.

<i>wt % in each phase</i> → ↓ <i>Compound</i>	Aq.	Org.	Aq.	Org.	Aq.	Org.
	Feed		Reaction 1		Reaction 2	
	92.5	60.8	91.7	56.0	85.8	56.7
	0.0	0.0	0.0	0.0	4.0	0.0
	7.5	39.2	6.3	31.5	4.1	24.6
	0.0	0.0	0.0	0.0	3.6	2.3
	0.0	0.0	2.0	12.5	0.0	0.0
	0.0	0.0	0.0	0.0	2.5	16.4
Total in each phase	100	100	100	100	100	100

still contain oxygen, and the only way to completely deoxygenate them is by using a second reactor operating in the organic phase or a high-temperature vapor phase hydrotreatment.

With solid-stabilized emulsions, a continuous process could be designed in which the two homogeneous phases coexist with the emulsion in a layered configuration: oil/emulsion/water. One can achieve full conversion on both sides of the emulsion followed by constant removal of oil-soluble products from the top layer and water-soluble products from the bottom layer while the reaction keeps occurring in the emulsion.

Our results highlight the preliminary applications of solid catalysts localized at the interface between two liquid phases. We anticipate that tailoring such emulsion-stabilizing solids with additional catalytic functional groups will facilitate a broad range of reactions.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/327/5961/68/DC1
Materials and Methods
SOM Text
Figs. S1 to S16
References

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Unveiling the Transient Template in the Self-Assembly of a Molecular Oxide Nanowheel

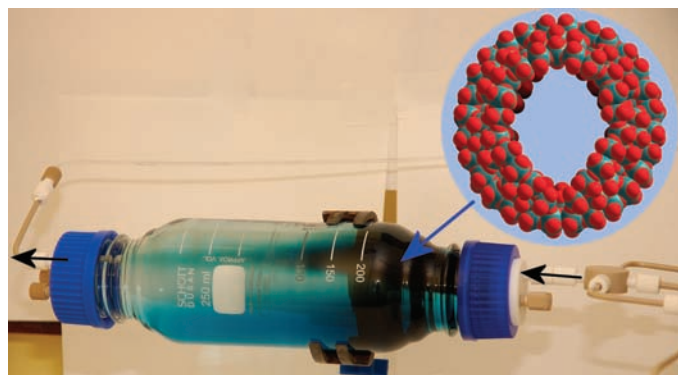
Haralampos N. Miras,¹ Geoffrey J. T. Cooper,¹ De-Liang Long,¹ Hartmut Bögge,² Achim Müller,² Carsten Streb,¹ Leroy Cronin^{1*}

Self-assembly has proven a powerful means of preparing structurally intricate nanomaterials, but the mechanism is often masked by the common one-pot mixing procedure. We employed a flow system to study the steps underlying assembly of a previously characterized molybdenum oxide wheel 3.6 nanometers in diameter. We observed crystallization of an intermediate structure in which a central {Mo₃₆} cluster appears to template the assembly of the surrounding {Mo₁₅₀} wheel. The transient nature of the template is demonstrated by its ejection after the wheel is reduced to its final electronic state. The template's role in the self-assembly mechanism is further confirmed by the deliberate addition of the template to the reaction mixture, which greatly accelerates the assembly time of the {Mo₁₅₀} wheel and increases the yield.

The bottom-up self-assembly of large inorganic architectures is a key synthetic route for the preparation of a whole range of systems from cages (1–3) to metal organic frameworks (4, 5) and the formation of macrocycles (6) from comparatively simple small molecule building blocks. In these systems the building blocks, and the underlying self-assembly processes, are understood to such a high degree that many complex and intricate structures can be designed from first principles, and the resulting architectures can even be

postsynthetically modified (7). However, when nanostructures in the 2- to 10-nm range are targeted (e.g., metallic nanoparticles and quantum

Fig. 1. A photograph of the flow-reactor system showing the blue reduction wavefront gradient formed within the vessel during the assembly of compound **1** (the reduced region is blue, and the more oxidized region is pale to clear). The structure of the {Mo₁₅₀} wheel present in compound **1** is shown in space-filling ball-and-stick mode. Mo ions are green spheres; O ligands are red spheres.



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dots), the self-assembly can be critically limited by the high number of degrees of freedom, and it is not trivial to target narrow size distributions. In contrast, in supramolecular chemistry, molecular templates have been successfully employed as external directors in the design of receptors (3, 8–10) and can facilitate the assembly of molecular nanostructures that are intrinsically monodisperse. Spectacular assembly control has been demonstrated by deliberate targeting and synthesis of templates that by design enable the formation of a predetermined structure, yet it is difficult to design large structures (2). The discovery of a similar templating strategy for the reliable fabrication of 2- to 10-nm molecular nanoparticles would revolutionize the synthesis and applications of molecular materials in the same way that templated synthesis has revolutionized the field of organic macrocyclic synthesis over the past 40 years.

In recent years, Müller and co-workers reported the solution-phase assembly of a family