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[15] Crystal structure data for **2b**: $C_{48}H_{90}Mo_6N_4O_{17}$, $M_r = 1570.88$, triclinic, $P\bar{1}$, $a = 12.4970(5)$, $b = 12.6163(5)$, $c = 20.5340(9)$ Å, $\alpha = 81.523(2)$, $\beta = 76.693(2)$, $\gamma = 76.237(2)°$, $V = 3045.4(2)$ Å^3, $Z = 2$, $Z' = 1$, $\rho_{calcd} = 1.713\ g\,cm^{-3}$, $T = 100(2)$ K, $R1 = 0.0395$, and $wR2 = 0.1083$. GOF (F^2) = 1.062. Crystal structure data for **2c**: $C_{56}H_{104}I_2Mo_6N_4O_{17}$, $M_r = 1394.87$, triclinic, $P\bar{1}$, $a = 16.3470(6)$, $b = 19.4509(7)$, $c = 22.6548(8)$ Å, $\alpha = 98.023(2)$, $\beta = 96.859(2)$, $\gamma = 90.465(2)°$, $V = 7079.6(4)$ Å^3, $Z = 4$, $Z' = 2$, $\rho_{calcd} = 1.815\ g\,cm^{-3}$, $T = 100(2)$ K, $R1 = 0.0369$, and $wR2 = 0.0964$. GOF (F^2) = 1.027. CCDC-187412 and -187413 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

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[18] ^{1}H NMR spectrum of the polymer: (400 MHz, [D$_6$]acetone, 25 °C): $\delta = 7.32$ (b, ArH, 4H), 7.10 (b, ArH, 2H), 4.04 (b, CH, 4H), 3.79 (b, OCH_2, 4H), 3.45 (t, $J = 6.25$ Hz, NCH_2, 16H), 1.81 (b, CH_2, 16H), 1.44 (m, CH_2, 16H), 1.34 (d, $J = 7.50$ Hz, (Ar-)CHMe_2, 24H), 1.17 (s, 18H, CH_3 in alkoxy chains), 0.97 ppm (t, $J = 7.37$ Hz, CH_3, 24H). UV/Vis (MeCN): $\lambda_{max} = 440$ nm.

[19] A small peak at 7.47 ppm in the ^{1}H NMR spectrum of the polymer is identified as arising from the end-group protons associated with the aromatic terminus. The integration of the peak at 7.47 ppm versus that at 7.32 ppm is 1:18. Assuming both ends of the polymer are capped by the iodo end group (as no acetylene proton resonance is observed in the NMR spectrum), this integration ratio gives the number of repeating units at 18.

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A Three-Phase Emulsion/Solid-Heterogenization Method for Transport and Catalysis**

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We describe a method for the heterogenization of (catalytic) reactions, which eliminates the need for organic solvents. The method relies on a novel multiphase transport concept, namely on the transport of hydrophobic substrates to an entrapped catalyst, and the transport of the resulting product from the catalyst-entrapping environment back into the bulk. The general idea is as follows: A catalyst is entrapped inside a hydrophobically modified porous sol-gel matrix; the hydrophobic substrate for that catalyst forms an emulsion in water in the presence of a suitable surfactant; and the powdered catalytic sol-gel material is dispersed in that emulsion. Upon contact of the surfactant with the hydrophobic interface of the sol-gel matrix, it reorients and spills the substrate into the pores of the matrix, where the catalyst is entrapped. The catalytic process takes place there, and the product is extracted out by the same transport vehicle, namely by the emulsifying surfactant; then the emulsion is broken, and the product separated.

We term this whole process the EST (emulsion–solid transport) process, and have demonstrated it (following a detailed search for optimal conditions) with the $[CH_3(C_8H_{17})_3N]^+[RhCl_4]^-$ catalyzed hydrogenation of chalcone and *cis*-stilbene, in which the solid is a partially alkylated SiO_2 sol-gel matrix within which the catalyst is entrapped, and where the emulsifying surfactant is cetyl(trimethylammonium) *p*-toluenesulfonate.

Heterogenization of homogeneous catalytic procedures has been of central interest in the field of catalysis. Several heterogenization methods have been developed[1] which can be classified into the following categories: Covalent-bond immobilization of the catalyst on supports such as inorganic matrices,[2] organic-polymer solids,[3] organic–inorganic composites,[4] and recently also on dendrimers[5] and liquid–liquid biphasic systems[6] in which the catalyst is in one phase and the product is in the other. Recent examples of such systems are fluorinated biphasic catalytic systems[7] and ionic liquids.[8] Other methods include supported liquid-phase catalysis (SLPC), which is based on immobilizing the catalyst within a thin liquid film on a high surface area support[9] and physical immobilization of the catalysts within porous supports, which requires no covalent bonding and which retains the homogeneous catalyst in its native structure. Sol-gel catalysis has been

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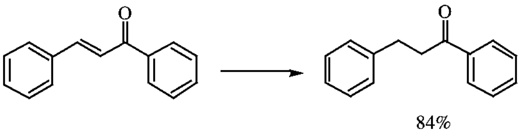
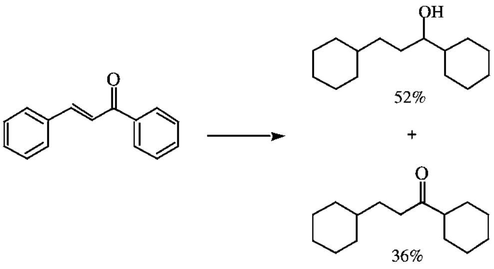
a prominent example of this approach, and is used in this study.[10] As we shall see below, the EST not only eliminates the need for organic solvents, but also opens up a new way of controlling the selectivity of catalysts.

Under the conditions described in the Experimental Section, emulsified chalcone was hydrogenated by the ethyl-derivatized, porous, solid catalytic material **1** (preparation and composition of all catalysts is described in the Experimental Section), to form the saturated ketone shown in 84% yield [Eq. (1)]. As suggested above, the emulsion acted as a vehicle for carrying the hydrophobic substrate to the alkylated solid, releasing its "cargo" there, and for carrying the product from the catalyst into the bulk solution within the same emulsion.



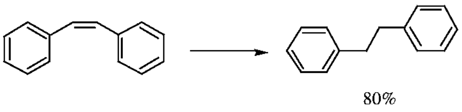
(1)

Interestingly, the catalytic activity was modified and enhanced by just changing the length of the alkyl chain of the alkyltrialkoxysilane. Thus, the octyl-derivatized catalyst **2** afforded 52% of the fully saturated 1,3-dicyclohexylpropan-1-ol accompanied by 36% of the 1,3-dicyclohexylpropan-1-one [Eq. (2)].

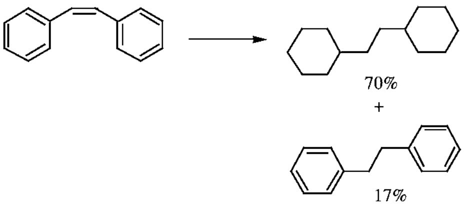


(2)

The alkyl-chain effect was also observed for the hydrogenation of *cis*-stilbene. While the short-chained **1** successfully hydrogenated the emulsified substrate to form 1,2-diphenylethane in 80% yield [Eq. (3)], the use of catalyst **2** resulted in 70% of the fully hydrogenated 1,1′-(1,2-ethanediyl)dicyclohexane [Eq. (4)].



(3)



(4)

Blank experiments were carried out to demonstrate that the successful transport of the substrate from the solution to the catalyst and of the product back into solution requires all the components of the EST system. Thus, with the non-alkylated catalyst **3** no product could be observed upon attempted hydrogenation of the emulsified *cis*-stilbene. In another blank experiment, in which catalyst **2** was used but without the emulsifying surfactant, catalysis did occur resulting in 43% 1,1′-(1,2-ethanediyl)dicyclohexane and 21% 1,2-diphenylethane, but without the convenience of the transport: The organic material was adsorbed into the hydrophobic sol-gel matrix (eventually poisoning the catalyst) and the product could be obtained only by organic-solvent extraction of the porous material.

The proposed mechanism of the EST process is best interpreted in terms of the well-studied behavior of adsorbed micelles.[11,12] Thus, several reversible processes (and one irreversible process) take place simultaneously (see Figure 1; S = substrate, P = product):

1. emulsified substrate + catalyst $\rightleftharpoons$ adsorbed surfactant + released/adsorbed substrate
2. adsorbed substrate $\rightarrow$ adsorbed product
3. adsorbed product + adsorbed surfactant $\rightleftharpoons$ emulsified product + solid

These equilibria are the key to the "communication" between the two phases: The first equilibrium is shifted by the catalytic reaction according to the Le Chatelier principle, while the third one is driven by the available adsorbed surfactant molecules.

An important feature of the EST is the possibility it opens up to change and affect the selectivity of the catalyst. The key is a careful control of the hydrophilic–lipophilic balance (HLB) of the solid itself. Thus, when the more hydrophobic catalyst **2** was used, the aromatic bonds in the substrates were reduced as well as the olefinic bond, while in the presence of the less hydrophobic catalyst **1**, only the olefinic bonds were

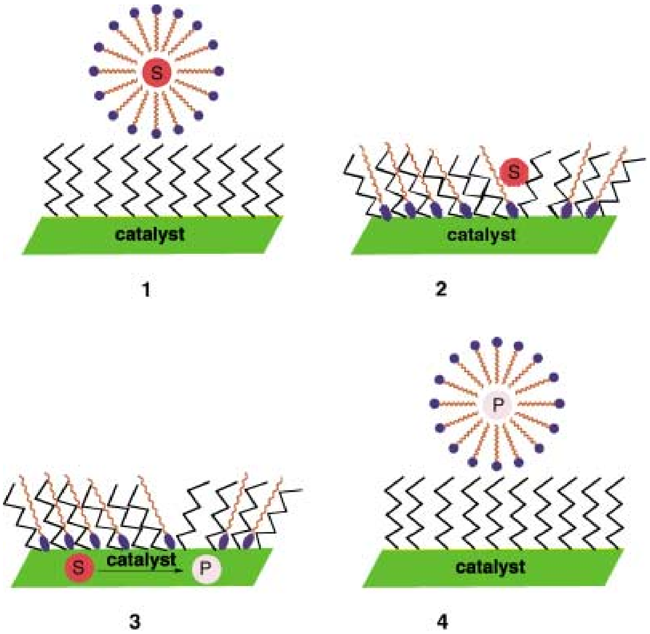


Figure 1. Illustration of the transport, reaction, and adsorption/desorption steps of the EST process. The emulsion which contains the substrate (**1**) spills its content into the catalyst material (**2**), the catalytic process takes place (**3**), and then the adsorbed surfactant carries the product back to the solution (**4**).

reduced. This different performance can be explained in terms of the proposed mechanism of EST. Thus, using the more hydrophobic interface facilitates the adsorption process of the hydrophobic substrate, leaving it in the vicinity of the entrapped catalyst longer, for fuller reduction.

Various degrees of alkylation of the matrix were tested, and the low ratio of alkylsilane:TMOS = 1:20 (tetramethylorthosilicate) gave the best results: Both higher and lower hydrophobicities gave inferior results; higher ratios caused the hydrophobic product to remain in the matrix, while lower ratios did not cause the emulsion to spill its content into the matrix. That so many silanols are still needed at the interface for the optimal EST process points to the possibility that the breaking of the micellar structures occurs mainly through adsorption of the ammonium head and, to a lesser degree, through interaction of the hydrophobic chain of the surfactant with the hydrophobic moieties on the surface. Indeed, the ethyl groups of **1** may be too short for such an interaction.

In conclusion, we have developed a new approach of heterogenization of catalysts, which is based on an aqueous three-phase system. Taking into account the intensive interest of replacing organic solvents with water even for hydrophobic reactants,[13] our EST process offers a new solution to that problem as well. Furthermore, in some recent papers[14] we have shown that sol-gel materials can be used, with the aid of surfactants, for tailoring a wide spectrum of reactivities of a single compound; here we provide a second example, in which the HLB of the sol-gel matrix can be used for that purpose as well. Finally, we believe that the EST approach will find applications beyond catalysis, because the concept demonstrated in Figure 1, coupled with chemical reactivity, is general.

Experimental Section

Preparation of the modified sol-gel entrapped catalysts **1** and **2**: A solution of ethyltriethoxyorthosilicate (0.36 mL, 1.68 mmol; ETOS) in EtOH (2.0 mL) was hydrolyzed by vigorous stirring with triply distilled water (0.12 mL; TDW) and hydrochloric acid (0.018 mL; 1M) at 60 °C for 20 h. The resulting solution was added to (5.0 mL, 33.6 mmol) of tetramethylorthosilicate {[ETOS]:[TMOS] = 1:20} that was prehydrolyzed with TDW (4.0 mL) at 25 °C for 2 h. Methyltrioctylammonium chloride (65 mg, 0.16 mmol; Aliquat 336) and $RhCl_3 \cdot 3H_2O$ (43 mg, 0.16 mmol) in MeOH (5.0 mL) was added to the combined solutions. Gelation occurred within 1–2 days and the resulting material was dried at 0.5 mm Hg for 24 h at 25 °C and for an additional 12 h at 78 °C. The xerogel formed was heated under reflux for 30 min with CH_2Cl_2 (20 mL), dried at 0.5 mm for 3 h, sonicated with the same solvent for 30 min, and dried again (3 h), which yielded the final ceramic catalyst **1** (2.64 g).

By a similar procedure, a homogeneous solution of TMOS (5.0 mL, 33.6 mmol) in TDW (4.0 mL; obtained by vigorous stirring of the mixture) and octyltrichlorosilane (0.39 mL, 1.68 mmol; OTS) was added to a solution of Aliquat 336 (65 mg, 0.16 mmol) and $RhCl_3 \cdot 3H_2O$ (43 mg, 0.16 mmol) in MeOH (5 mL). The mixture was stirred until gelation occurred (3–4 days), and the gel treated as above, which resulted in **2** (2.7 g).

For control-experiment comparison, the non-alkylated sol-gel catalyst **3** was prepared, as follows: A solution of TMOS (5.0 mL, 33.6 mmol) was stirred with TDW (4.0 mL) for 2 h until homogenous, and then Aliquat 366 (65 mg, 0.16 mmol) and $RhCl_3 \cdot 3H_2O$ (43 mg, 0.16 mmol) dissolved in MeOH (5.0 mL) were added, and the solution stirred until gelation occurred (1–2 days). The resulting gel was treated as described above, to yield 2.38 g of ceramic material.

Emulsion experiments*:* The oil-in-water (O/W) emulsion was prepared by adding the oil phase (chalcone (1.0 g, 4.8 mmol) or *cis*-stilbene (1.0 mL, 5.6 mmol) both dissolved in 2.0 mL heptane) dropwise to a vigorously stirred solution of surfactant (2 % w/w) in water (15.0 mL). Vigorous stirring was continued for 5 min and resulted in a stable emulsion when cetyl(trimethylammonium) *p*-toluenesulfonate was used. Other surfactants which were tested (cetyl(trimethylammonium) bromide, sodium dodecylsulfate, Tween 80, and Tween 20) were inferior either for the emulsification or for the catalytic process.

After the catalytic reaction was stopped, the filtered emulsion of the products and the unreacted starting material was broken by adding of 5 % sodium sulfate (10.0 mL) and heating the mixture in a closed vial at 80 °C for 24 h, (until full separation of the two phases). Occasionally it was necessary to add another salt (NaCl) to obtain complete separation. If the surfactant was used in excess of 2 % w/w, the resulting emulsions were difficult to break. Finally, it should be noted that we could extract the organic material from the emulsions with organic solvents, but our efforts were mainly directed toward methods which avoid these solvents.

The catalytic reactions*:* The above emulsion containing either chalcone or *cis*-stilbene and catalytic material (0.9 g) was placed in a 50-mL glass-lined stainless-steel autoclave. After sealing the reaction vessel, it was purged with hydrogen three times, pressurized to 200 psi of H_2 and heated at 80 °C for 20 h with magnetic stirring. The autoclave was cooled to room temperature and the hydrogen was released. The catalyst was then separated from the emulsion by filtration and the emulsion broken as described above. The products—all known—were characterized by GC, GC–MS, and NMR spectroscopy.

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