

Three-Phase Microemulsion/Sol–Gel System for Aqueous Catalysis with Hydrophobic Chemicals

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Abstract: A facile three-phase transport process is described that allows to carry out catalytic reactions in water, whereby all components are hydrophobic. According to this process a hydrophobic substrate is microemulsified in water and subjected to an organometallic catalyst, which is entrapped within a partially hydrophobized sol-gel matrix. The surfactant molecules, which carry the hydrophobic substrate,

adsorb/desorb reversibly on the surface of the sol-gel matrix breaking the micellar structure, spilling their substrate load into the porous medium that contains the catalyst. A catalytic reaction

Keywords: heterogeneous catalysis • hydrogenation • microemulsion • sol-gel processes • three-phases transport

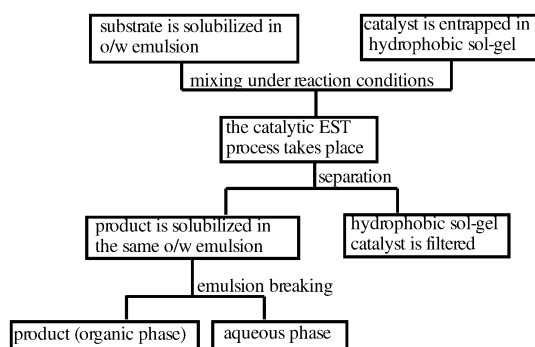
then takes place within the ceramic material to form the desired products that are extracted by the desorbing surfactant, carrying the emulsified product back into the solution. The method is general and versatile and has been demonstrated with the catalytic hydrogenations of alkenes, alkynes, aromatic C=C bonds, and nitro and cyano groups.

Introduction

The three-phase emulsion/solid transport process: In this study, we have merged two domains, each of which proved to be very useful and fruitful for the general field of catalysis. One domain is the application of sol-gel materials^[1] as heterogeneous carriers of catalysts,^[2] and the other is the use of microemulsions for solubilization.^[3] We show that by the careful combination of these two methodologies, one can carry out catalytic reactions in water, whereby both the catalyst and its substrate are hydrophobic. Since the majority of catalytic reactions involve hydrophobic components, a general method that allows the replacement of the traditionally required organic solvents by water, may become useful when environmental issues are to be considered.^[4]

Towards this goal we developed recently a novel and general approach that eliminates the need of organic solvents in

hydrophobic heterogeneous catalysis (and in fact in heterogeneous reactions in general).^[5] It relies on a three-phase emulsion/solid transport (EST) method illustrated in Scheme 1. The hydrophobic substrate is emulsified in water



Scheme 1. A flow-chart of the emulsion/solid transport three-phase process. The advantageous microemulsion process follows similar steps.

(an oil-in-water (o/w) emulsion) with a carefully selected surfactant and then is subjected to the (organometallic) catalyst, which is entrapped within a partially hydrophobized sol-gel matrix. The surfactant molecules that carry the hydrophobic substrate adsorb/desorb reversibly on the surface of the sol-gel matrix,^[5] breaking the micellar structure^[6] and spilling their substrate load into the porous medium that contains the metal-complex catalyst. A catalytic reaction then takes place within the ceramic material to form the de-

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sired products that are extracted by the desorbing surfactant, carrying the emulsified product back into the solution. The free products are finally obtained by breaking the emulsion.

A major improvement we introduce here to this EST process, and which we recommend as a standard procedure over our previously reported procedure,^[5] is to move from an emulsion to a *microemulsion*. We recall that microemulsions are defined as thermodynamically stable and optically transparent macroscopically homogeneous mixtures of oils, water, and surfactants.^[3,7] Being based on aqueous media they are economically favored and environmentally safer than conventional organic solvents, while overcoming reagent incompatibility with water. Microemulsions have been used as microreactors,^[8] and, owing to their large interfacial area, were found to accelerate chemical processes and to induce regioselectivity in organic reactions as a function of their composition.^[9] Microemulsions have also been used in various catalytic processes. Examples include oxidation,^[10] hydroformylation,^[11] carbonylation,^[12] dehalogenation,^[13] and free-radical chain polymerization.^[14] In the application to the three-phase catalysis reported herewith the o/w microemulsion is used as a carrier of *both* the substrate and the product. Since the catalysis takes place within the non-soluble ceramic component of the system, it can be filtered off and re-used. There are several advantages of replacing the regular emulsion by a microemulsion in the EST method.

- 1) Temperature flexibility: a whole range of convenient temperatures can be used (as opposed to the narrow window around 80 °C needed for the regular emulsion method^[5]).
- 2) A wider range of surfactants can be used (unlike the regular emulsion described in our previous study,^[5] which we could affect only with cetyl(trimethylammonium) 4-toluenesulfonate).
- 3) The large surface area of the microemulsion makes the transport process into and out of the solid more efficient.

Since the EST methodology involves several equilibria which take place in a rather complex system, the main art that had to be practiced is the tailoring of the right HLB (hydrophilic/lipophilic balance) of both the surfactant and the solid matrix. The micro-EST (for short, we shall continue to use EST for microemulsions as well) systems described below are composed of either anionic surfactants (sodium dodecylsulfate (SDS), sodium 4-dodecylbenzenesulfonate (SDBS)) or cationic surfactants (cetyltrimethylammonium bromide

(CTAB), *N,N*-dimethyl-*N*-dodecyl-*N*-(2-hydroxyethyl)ammonium bromide (DDHAB)); and of partially hydrophobically derivatized silicas, namely octylated and phenylated sol-gel matrices. The catalysts $[(\text{CH}_3)(\text{C}_8\text{H}_{17})_3\text{N}]^+[\text{RhCl}_4]^- \cdot n\text{H}_2\text{O}$ and $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+\text{PF}_6^-$ were entrapped within these matrices (and, for comparative purposes, $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+\text{PF}_6^-$ was also entrapped in hydrophilic silica) and used for the selective hydrogenation of unsaturated hydrophobic substrates.

Experimental Section

Chemicals: $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+\text{PF}_6^-$ ^[15] and *N,N*-dimethyl-*N*-dodecyl-*N*-(2-hydroxyethyl)ammonium bromide^[16] were synthesized according to published procedures. All other chemicals are commercial.

Microemulsification procedures: Two general procedures were employed for the microemulsification of the various substrates.

Procedure A: A mixture of an appropriate surfactant (1.0–1.4 g) in triply distilled water (TDW; 10 mL) and the organic substrate (9.7–24 mmol) was emulsified by vigorous stirring. The resulting emulsion was then titrated with either *n*-butanol or *n*-amyl alcohol (typically, 2–5 mL) until a clear transparent microemulsion was obtained. In case the exact endpoint had been passed by excess alcohol (turbidity appears), back-titration was carried out by adding more of the surfactant. The solution was then sonicated for 5–10 min. (A simple test for a successful microemulsification, in addition to its transparency, is the shining of the light of a laser pointer through the solution: the beam is clearly seen.) The microemulsions so formed proved stable at the reaction temperatures of 80–100 °C. Breaking of the emulsion at the end of the reaction was achieved by agitation with NaCl (0.2 g). If during the emulsification foam was formed, sonication for 20 minutes solved this problem.

Procedure B (suitable in particular for polycyclic arenes): The substrate (4–9 mmol) dissolved in either methylcyclohexane (2.0 mL) or warm butanol (3.0 mL) was added to a stirred solution of SDS (3–4 mmol) in TDW (10 mL); the resulting emulsion was heated to 60 °C and titrated with *n*-butanol (2–3 mL) to form the transparent microemulsion. It was then sonicated for 5 min. Representative data for the formation of microemulsions with several substrates are summarized in Table 1.

Entrapment of the catalysts in organically modified sol-gel matrices

Catalyst I: A solution of octyltriethoxysilane (2.1 mL, 6.72 mmol) in EtOH (5.6 mL, 95.6 mmol) was hydrolyzed by TDW (0.36 mL) at 84 °C for 4 d. The resulting solution was added to a mixture of tetramethoxysilane (TMOS, 5.0 mL, 33.6 mmol) and TDW (4 mL) and stirred for 1 h (the molar ratio octyltriethoxysilane:TMOS is 1:5). A solution of $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+\text{PF}_6^-$ (40 mg, 0.0454 mmol) dissolved in a mixture of

Table 1. Composition of representative microemulsions

Entry	Substrate (%) ^[a]	Surfactant (%) ^[b]	Percentage of <i>n</i> -butanol	Percentage of water
1	1-octene (10.1)	DDHAB (8.2)	11.4	70.3
2	1-octene (9.6)	SDS (7.8)	15.3	67.3
3	1-hexene (12.3)	SDS (7.3)	19.7	60.7
4	1-undecene (10.4)	CTAB (6.9)	13.5 ^[c]	69.2
5	styrene (9.4)	DDHAB (8.3)	11.3	71.0
6	phenylacetylene (9.8)	DDHAB (9)	6.1	75.1
7	ethylbenzene (11.2)	SDBS (8.4)	15.7	64.7
8	naphthalene (3.0)	SDBS (7.7)	15.4 ^[d]	59.6
9	nitrobenzene (13.7)	SDBS (7.5)	21.4	57.4
10	diphenylamine (8.8)	SDBS (8.2)	24.3	58.7
11	benzointrile (12.2)	SDBS (7.8)	19.6	60.4

[a] Except for the microemulsions of naphthalene and diphenylamine that were prepared by procedure B, all others were prepared by procedure A. [b] DDHAB: *N,N*-dimethyl-*N*-dodecyl-*N*-(2-hydroxyethyl)ammonium bromide, SDS: sodium dodecylsulfate, CTAB: cetyltrimethylammonium bromide, SDBS: sodium 4-dodecylbenzene sulfonate. [c] *n*-Pentanol was used here. [d] And 14.3% methylcyclohexane.

acetone (2 mL) and THF (8 mL) was added. After stirring for 5 min a solution of 0.1 M tetrabutylammonium fluoride (0.2 mL) in THF was added. Gellation occurred within 1 h. The resulting material was dried at 0.5 mm for 24 h at 54 °C; the so-formed xerogel was treated with CH_2Cl_2 (20 mL) under reflux for 30 min. The material was dried at 0.5 mm for 3 h, sonicated with the same solvent for 30 min and dried again (3 h). The final weight of the ceramic catalyst, $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+\text{PF}_6^- @ (\text{C}_8\text{H}_{17})\text{-SG}$, (catalyst **1**), was 3.9 g and the catalyst loading was $0.0116 \text{ mmol g}^{-1}$. No detectable leaching of the entrapped catalyst was evident neither in **1** nor in the catalysts described next.

Catalyst 2: For comparative purposes, $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+\text{PF}_6^-$ was also entrapped in hydrophilic silica sol–gel matrix by the following procedure. A solution of TMOS (5.0 mL, 33.6 mmol) and TDW (4 mL) in EtOH (5.6 mL) was stirred for 1 h. A solution of $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+\text{PF}_6^-$ (40 mg, 0.0454 mmol) in a mixture of acetone (2 mL) and THF (8 mL) was added. After stirring for 5 min a solution of 0.1 M of tetrabutylammonium fluoride (0.2 mL) in THF was added and gellation occurred within 15 min. The resulting gel was treated as described for catalyst **1** to give 2.8 g of $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+\text{PF}_6^- @ \text{SG}$ (catalyst **2**). The catalyst loading was $0.0162 \text{ mmol g}^{-1}$.

Catalyst 3: A solution of phenyltrimethoxysilane (0.63 mL, 3.37 mmol) in EtOH (2.0 mL) was hydrolyzed with TDW (0.18 mL) by heating the solution at 60 °C for 24 h. The resulting solution of the hydrolyzed silane was added to a stirred solution of TMOS (5.0 mL, 33.6 mmol; molar ratio of phenyltrimethoxysilane:TMOS is 1:10), TDW (4.0 mL), methyltriocetylammmonium chloride (65 mg, 0.16 mmol) and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (43 mg, 0.16 mmol) dissolved in MeOH (5.0 mL). The combined solutions were stirred for 5 min and then a solution of 0.1 M tetrabutylammonium fluoride in tetrahydrofuran (0.2 mL) was added. Stirring was continued until the mixture gelled (2–3 d). The resulting material was dried at 0.5 mm for 48 h at room temperature and then treated as above with CH_2Cl_2 , yielding 2.95 g of $\{[(\text{CH}_3)(\text{C}_8\text{H}_{17})_3\text{N}]^+[\text{RhCl}_4]^- @ (\text{C}_6\text{H}_5)_3\text{-SG}$, (catalyst **3**). The catalyst loading was $0.0542 \text{ mmol g}^{-1}$.

Catalyst 4: This catalyst was prepared similarly to catalyst **3**, except that the hydrophobic silane monomer used was octyltrimethoxysilane (0.43 mL, 1.664 mmol, octyltrimethoxysilane:TMOS = 1:20), which was hydrolyzed with TDW (0.09 mL) in ethanol (2.0 mL) at 60 °C for 24 h. An amount of 2.75 g of the ceramic catalyst, $\{[(\text{CH}_3)(\text{C}_8\text{H}_{17})_3\text{N}]^+[\text{RhCl}_4]^- @ (\text{C}_8\text{H}_{17})\text{-SG}$, (catalyst **4**), was obtained. The catalyst loading was $0.0581 \text{ mmol g}^{-1}$.

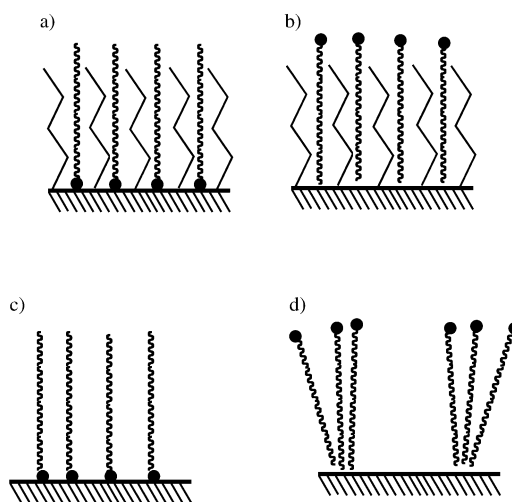
The catalytic reactions: A freshly prepared microemulsion (typically 15–20 mL) with the appropriate substrate (in the range of 3.6–24 mmol), prepared according to either procedure A or B, was added to the catalytic material (typically in the range of 0.02–0.08 mmol rhodium complex) in a 50 mL glass-lined stainless-steel autoclave equipped with a magnetic stirrer and a sampling device. After sealing the reaction vessel, it was purged three times with hydrogen, pressurized to 200 psi H_2 and heated with stirring at 80 °C for the required length of time. Upon completion of the reaction, the autoclave was cooled to room temperature and unsealed. The ceramic catalyst was separated from the reaction mixture by filtration and the microemulsion broken by adding NaCl as described above. The resulting two phases were separated, the organic phase was worked up in the usual manner and the resulting products analyzed by GC-MS, GC, and NMR spectroscopy. All products are known and were compared with authentic samples. For re-use, the catalyst was refluxed in MeOH (20 mL) for 30 min, dried at 0.5 mm for 3 h at room temperature, sonicated with CH_2Cl_2 (20 mL) for 30 min and dried again at 0.5 mm for 2 h at room temperature.

Results and Discussion

Hydrogenation of 1-octene: $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+\text{PF}_6^-$ entrapped in octylated silica (prepared from a 1:5 molar ratio of octyltriethoxysilane/TMOS; catalyst **1**) promoted quantitative transformation (98%) of a microemulsion of 1-octene (see entry 1 in Table 1), to *n*-octane within 4 h under the conditions given in the Experimental Section. Lower molar

ratios (lower hydrophobicities) were tested as well. Thus, 1:20, 1:15 and 1:10 molar ratios yielded *n*-octane and unhydrogenated isomerization products at ratios of 89:9.5, 92:7 and 95:4%, respectively.

As mentioned above, an advantage of the microemulsion approach over the emulsion approach is the possibility to employ a wider range of surfactants. Thus, in addition to the cationic surfactant DDHAB, we were able to hydrogenate 1-octene in a microemulsion prepared with an anionic surfactant. When 1-octene was microemulsified in the presence of sodium dodecyl sulfate (SDS) (entry 2, Table 1), the hydrogenation with catalyst **1** yielded 96% of *n*-octane (along with just 2% of isomerization products). One may wonder how it is possible that both types of surfactants are suitable for the EST process. As is well known,^[6] the cationic and anionic surfactants adsorb differently on the partially hydrophobic silica surface (Scheme 2 a,b), namely with the cation-



Scheme 2. Illustration of the adsorption of surfactants: a) a cationic surfactant on a partially hydrophobic silica surface; b) an anionic surfactant on a partially hydrophobic silica surface; c) a cationic surfactant on a hydrophilic silica surface; d) an anionic surfactant on a hydrophilic silica surface.

ic head pointing to the surface or the anionic head pointing away from the surface, respectively. However, the final outcome is similar for the EST purpose: Reversible rupture of the (hemi)micellar^[6] structure, spilling its content into the porous material, or collecting the product from it.

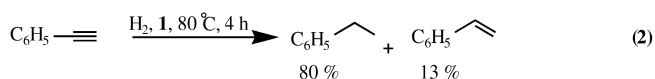
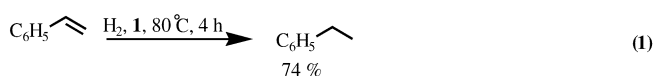
When—for comparative purposes— $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]^+\text{PF}_6^-$ was entrapped in the nonhydrophobized silica sol–gel matrix (catalyst **2**) and used for the hydrogenation of 1-octene (80 °C and 200 psi of H_2) in heptane as solvent, 63% of *n*-octane and 37% of isomerization products were obtained after 4 h (compared to the hydrogenation by catalyst **1** under the microemulsion conditions which produced, as described above, *n*-octane in an almost quantitative yield). Thus, under these “standard” organic-solvent conditions, the isomerization products do not reside long enough within the hydrophilic catalytic material to be converted to *n*-octane. Similar results, but with some improvement, were obtained

with the hydrophilic catalyst **2** when heptane was replaced by the cationic (DDHAB) microemulsion: a fast reaction took place (full conversion within 4 h); however, again substantial isomerization competed with the hydrogenation process [29% of isomerization products (*cis*- and *trans*-2-octene and *trans*-3-octene) and 70% *n*-octane].

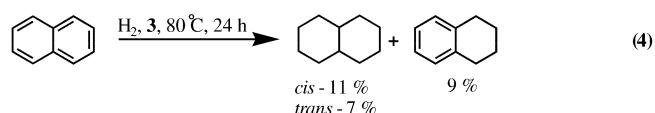
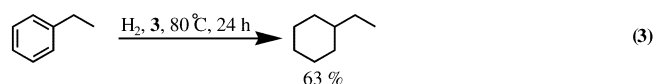
It can be concluded therefore that the process of hydrophobization of the silica surface by surfactant adsorption is less efficient than the hydrophobization by partial surface derivatization (catalyst **1**). The existing hydrophobic chains on catalyst **1** interact with the chains of the cationic surfactant, promoting its adsorption. Interestingly, however, when the *anionic* SDS microemulsion was used with catalyst **2**, the percentage of full reduction to *n*-octane increased to 90 (along with 10% of isomerization). We are currently in a position to only speculate as to the origin of this surprising apparent pronounced hydrophobization. When a cationic micelle opens and adsorbs, the individual surfactant molecules are dispersed on the surface (Scheme 2c) in a way that follows the dispersion of the silanols (about 4–5 silanols nm⁻²[17]). However, when anionic surfactant molecules adsorb, heterogeneous clusters of hydrophobic chains are energetically preferred over homogeneous dispersion, and, thus, on a local microscopic level, adsorbed anionic surfactants form islands of pronounced hydrophobicity (Scheme 2d); this facilitates the EST process at these sites.

Hydrogenation of other alkenes and alkynes: 1-Hexene and 1-undecene were hydrogenated best in microemulsions by [(CH₃)(C₈H₁₇)₃N]⁺[RhCl₄]⁻·*n*H₂O entrapped in octylated silica sol–gel (catalyst **4**). 1-Hexene was microemulsified as specified in entry 3 (Table 1). After 6 h under the conditions given in the Experimental Section, 90% of the hexene was converted into alkene-free *n*-hexane. Unlike 1-hexene and 1-octene, 1-undecene could be neither microemulsified by SDS nor by DDHAB, but required a surfactant with a longer chain, such as cetyltrimethylammonium bromide. It is also worth noting the fact that *n*-butanol proved unsuitable as the co-surfactant in this system, but *n*-amyl alcohol led to the formation of a stable microemulsion (entry 4, Table 1) that afforded a quantitative yield of pure undecane after a 4 h period of hydrogenation.

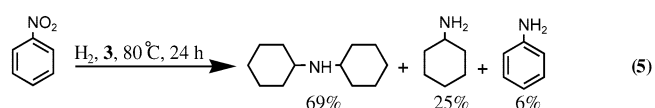
Alkenes and alkynes substituted by aromatic moieties could be microemulsified by the same procedure as employed for octene. The amount of co-surfactant required for these substrates was, however, smaller than that needed for the non-aromatic alkenes (see, for example, entries 5 and 6, Table 1). The microemulsified styrene was smoothly hydrogenated to ethylbenzene [74% within 4 h, Eq. (1)] and microemulsified phenylacetylene formed, in a stepwise way, styrene and ethylbenzene [Eq. (2)].



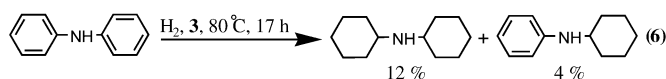
Hydrogenation of the aromatic ring: Ion pair [(CH₃)(C₈H₁₇)₃N]⁺[RhCl₄]⁻·*n*H₂O entrapped in a phenylated silica sol–gel matrix (catalyst **3**) was found most suitable for the EST hydrogenation of the aromatic C=C bonds of ethylbenzene. Structural similarity between the component of the catalyst and the substrate seems to be necessary for successful catalytic reactions in the EST system. In fact the hydrogenation of the arene was found to proceed best when the surfactant contained a phenyl ring as well (cf. the requirement of a longer surfactant for the long chained 1-undecene than that for 1-octene). Thus, ethylbenzene was microemulsified with SDS (entry 7, Table 1). Naturally, the arene ring hydrogenation proceeded slower than the saturation of the above-mentioned alkenes, so that ethylbenzene afforded 63% of ethylcyclohexane (as the only reaction product) after 24 h under the conditions described in the Experimental Section [Eq. (3)]. Aromatic polycyclics reacted even slower. For example, the microemulsion of naphthalene (entry 8, Table 1) gave after 24 h at 80 °C only a mixture of 9% tetralin, 11% of *cis*- and 7% of *trans*-decalin [Eq. (4)].



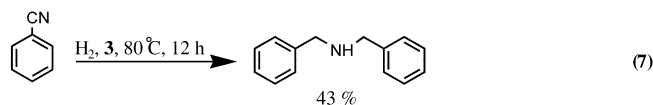
Hydrogenation of the nitro and cyano moieties: The EST methodology was also applied to the hydrogenation of nitro and cyano moieties. The microemulsion described in entry 9 (Table 1) was hydrogenated gradually to give initially aniline (after 13 h at 80 °C 98% of aniline was isolated), which was further transformed to cyclohexylamine and dicyclohexylamine. The latter becomes finally the major product. After 24 h the mixture of products consisted of 69% dicyclohexyl-



amine, 25% cyclohexylamine, and 6% aniline, [Eq. (5)]. Diphenylamine seems not to be a reaction precursor of dicyclohexylamine. Careful continuous analysis of the reaction neither revealed any traces of this compound nor of its partial hydrogenation products. The hydrogenation of diphenylamine listed in Table 1 (entry 10) is slow and affords after 17 h 12% of dicyclohexylamine and 4% of phenylcyclohexylamine [Eq. (6)].



The hydrogenation of a microemulsion of benzonitrile, (see entry 11) afforded after 12 h in the presence of catalyst **3** 43% of dibenzylamine [Eq. (7)]. We recall that the ion



pair $[(\text{CH}_3)(\text{C}_8\text{H}_{17})_3\text{N}]^+[\text{RhCl}_4]^- \cdot n\text{H}_2\text{O}$ encapsulated in a hydrophilic sol-gel promotes hydrogenation of nitrobenzene and benzonitrile to give mainly aniline and benzylamine, respectively.^[18] Here we observed that modification of the sol-gel matrix with the hydrophobic group changes the selectivity of the catalyst. (Modification of selectivity was also observed in the regular emulsion system.^[5])

Finally, it should be noted that in all of the hydrogenation catalyses we were able to recover the solid-state components of the system simply by filtration and re-use the catalyst for three consecutive runs.

In conclusion, we have shown the versatility of the three-phase emulsion-surface transport (EST) methodology by utilizing microemulsified substrates. The concept is general and we believe that carrying out many-hydrophobic reactions in aqueous media will prove feasible and be of economical and environmental benefit.

Acknowledgement

This work was supported by the Ministry of Science, Art, and Sport through the Tashtiot project and by the Israel Science Foundation through Grant No. 143/00-12.0.

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Received: October 1, 2003 [F5591]