Colloid Polym Sci 274:261–268 (1996)
© Steinkopff Verlag 1996

ORIGINAL CONTRIBUTION

H.N. Flach
I. Grassert
G. Oehme
M. Capka

New insoluble surfactant systems as aids in catalysis. A convenient method for nonbonded immobilization of catalytically active transition metal complexes

Received: 6 February 1995
Accepted: 3 September 1995

H.N. Flach · I. Grassert · G. Oehme (✉)
Institut für Organische Katalyseforschung
an der Universität Rostock e.V.
Buchbinderstraße 5–6
18055 Rostock, FRG

M. Capka
Institute of Chemical Process Fundamentals
Rozvojová 135
165 02 Prague 6, Czech Republic

Abstract New insoluble surface-active substances are described here for the first time. They were synthesized by esterification of the surfactants sodium 11-hydroxy-undecane-1-sulfonate or dodeca-ethylene glycol monododecyl ether with an aliphatic amino acyl chloride, reaction of the amino group containing ester with the bifunctional reagent 3-(triethoxysilyl) propyl isocyanate, and anchoring the products obtained on silica 100 under mild conditions.

The surfactants thus immobilized showed a micellar effect, as proved by their influence on reaction rate and selectivity in the enantioselective hydrogenation of methyl (*Z*)-α-acetamido-cinnamate to methyl *N*-acetyl-phenylalaninate (*R*) by means of an optically active rhodium complex in water.

The systems were compared with an inorganic ion exchanger with dodecyl sulfate counterions and with sodium dodecyl sulfate adsorbed to alumina. The influence of the immobilized surfactants on reaction rate and selectivity appeared to be dependent on the mobility of the hydrophobic chains.

Key words Silica – surfactants – immobilisation – polyethylene glycol dodecyl ether – phase-transfer

Introduction

Surfactants appear to have an advantageous effect on the asymmetric hydrogenation in water of amino acid precursors such as methyl (*Z*)-α-acetamidocinnamate by means of optically active rhodium (*I*) complexes: from previous experiments it was concluded that these hydrogenations could be carried out in organic solvents, e.g., methanol, as well as in aqueous surfactant dispersions [1, 2]. A change to polymeric surfactants (polysoaps) should bring advantages in the product work-up. Several types of amphiphilized polymers were tested: the best results were obtained with ionic surfactants, immobilized as counterions onto macroreticular ion exchangers. These amphiphilic counterions had almost the same effect on the hydrogenation as micelles formed by unbound surfactants [3]. Preferably the support should be very rigid for optimal effects. In order to broaden the understanding about insoluble surfactant systems, we intend to present the synthesis and properties of surfactants immobilised onto silica or alumina in this paper.

The adsorption of surfactants on inorganic solid phases is a current topic of research: Couzis [4] studied the interaction of sodium dodecanoate with alumina by means of IR-ATR and found that this amphiphile adsorbed irreversibly. Using ^{2}H-NMR, Söderlind [5] demonstrated that the most likely structure of SDS, adsorbed onto alumina in water, is a bilayer. A bilayer structure was also indicated by the plateau adsorption level and calculated surface density of didodecyldimethylammonium chloride onto various silicas at pH 10 [6]. Such a structure, having a hydrophobic core and a hydrophilic surface, might show the same properties as micelles dispersed in water.

In order to facilitate the work-up of micelle-catalysed reaction product, Yu [7] investigated the possibility of catalyzing the hydrolysis of trimethyl orthobenzoate in water with alumina-adsorbed SDS bilayers. It was shown that this heterogeneous catalytic system worked analogously to free SDS. However, though the authors state that surfactant leaching from alumina should be negligible, no proof was given that the hydrolyzed product could be obtained in pure (surfactant-free) form.

We are interested in immobilizing catalytic metal complexes on solids by means of entrapment in a hydrophobic surface layer. Much research has been done to immobilize metal complexes covalently onto solids [8–10]. Normally, a loss in their reactivity is observed upon immobilization. We expected this loss to be smaller when the catalyst is not covalently fixed but only included in an amphiphilic environment. The pathway used to immobilize surfactants onto silica was already described for a silica-based phase transfer catalyst [11].

The importance of immobilized surfactants might reach beyond the goal aimed at here, e.g., for micellar reversed-phase liquid chromatography [12] or in the oxidation of styrene to benzophenone in micellar environments [13]. An interesting application for surfactant-containing silica was given by Waddell et al. [14], who polymerized styrene and butadiene in adsorbed tenside layers on silica. Thus, silica with an improved rubber compatibility was obtained which could be used as tire rubber reinforcer.

Experimental

Materials

2-Aminoethanoic acid (glycine), obtained from Reachim, Russia, was dissolved in hot water, precipitated with cold ethanol, washed with ether and dried in vacuo at 110 °C in order to obtain a very fine powder. 4-aminobutanoic acid (Merck) was used as received. Dodecaethyleneoxide monododecyl ether ($E_{12}C_{12}$, Sigma) was purchased as decaethyleneoxide monododecyl ether ($E_{10}C_{12}$). Elemental analysis indicated a somewhat higher mean oligomericity: found C 60.18, H 10.40 ($E_{12}C_{12}$: $C_{36}H_{74}O_{13}$ calc. C 60.48, H 10.43, $E_{10}C_{12}$: $C_{32}H_{66}O_{11}$ calc. C 61.31, H 10.61). Mass spectrometry indicated a broad molecule size distribution of up to $E_{16}C_{12}$.

3-(triethoxysilyl) propyl isocyanate was purchased from ABCR, Karlsruhe, Germany, and distilled before use. Silica 100 and alumina 90 of activity II–III, both of granular size 0.063–0.2 mm, were supplied by Merck. The silica was dried at 100 °C/1 Torr. Wofatit OK 80 (Farbenfabrik Wolfen – marketed by Bayer- macroreticular resin with sulfonic acid groups) was methanol-washed and dried at 60 °C. Sodium dodecyl sulfate (SDS, Merck) and cetylethyldimethylammonium bromide (Aldrich) were used as received. THF, toluene, benzene and dioxane were dried with sodium in the presence of benzophenone until the liquid coloured blue, and distilled. Ether was stored over Na, dichloromethane over $MgSO_4$. *N*,*N*-dimethylacetamide (DMA, Fluka) was stored over $MgSO_4$ and an acrylic ion exchanger. Triethylamine and pyridine were dried over KOH, and distilled. The rhodium complex used was [Rh(COD) BPPM]BF_4 [1]. (COD is 1,5-cyclooctadiene and BPPM is (2S,4S)-*N*-tertbutoxycarbonyl-4-diphenylphosphino-2-diphenylphosphinomethyl-pyrrolidine).

Methods

NMR spectra were made with a Bruker 250 or 400 MHz spectrometer. Elemental analysis was carried out with a Leco CHNS 932 automatic analyzer. δ-values are given in ppm with tetramethylsilane as standard. The rhodium contents were measured by UV-VIS after digestion with $KHSO_4$ and complexation with $SnCl_2$. FT-IR-spectroscopy was done with a Nicolet Magna 550 spectrometer (in KBr pellets). Enantioselective analysis was carried out with an HP 5890 Series II gas chromatograph on a 10 m capillary quarz column coated with XE 60 L-valin-tert-butylamide (FID, split 1: 60, 150 °C). For the surface determination a Micrometrics ASAP 2400 BET apparatus was used at − 196 °C with pressures between 7 and 760 Torr. The error in the result is smaller than 5%.

The hydrogenation procedure was described elsewhere [3]. In short: oxygen-free water, surfactant, substrate, rhodium complex and chiral phosphine ligand (usual mole ratio rhodium : surfactant : substrate = 1:20:100) were placed in a deaerated hydrogenation flask under argon and stirred for 20 h at room temperature. A hydrogen atmosphere at normal pressure was set and the hydrogen consumption monitored volumetrically. After reaction, 20 ml of water was added and the mixture stirred for 30 min, the polymeric surfactant allowed to sedimentate and ca. 20 ml of the transparent solution then separated to be extracted with chloroform. In case of reuse of the immobilized catalyst, new substrate was added and the reaction repeated.

Glycyl chloride hydrochloride (***1a***) [*15*]

Glycine (7.3 g, 0.097 mol) was dispersed in 80 ml of freshly distilled tetrachloromethane and phosphorpentachloride

(29.6 g, 0.14 mol) was added. After stirring for 20 h at 30 °C and 20 h at 20 °C, the white crystalline product was filtered off and washed with dry ether. Recrystallization in acetyl chloride [16] appeared impossible. Yield 6.8 g (54%). Elemental analysis: found (calculated $C_2H_2NOCl_2$): C 20.12 (18.48), H 3.99 (3.88), N 11.54 (10.78), Cl 47.6 (54.55). The analysis indicates that the chloride is mixed with the starting amino acid or its oligopeptide. However, it could be used without further purification.

Alternatively, an analogous synthesis of 3-aminopropanoyl chloride hydrochloride in acetyl chloride was possible, which gave a purer product that could be used analogously. Elemental analysis: found (calculated $C_3H_7NOCl_2$): C 25.06 (25.02), H 4.79 (4.90), N 7.46 (7.53), Cl 48.8 (49.25).

*11-(2-Aminoethanoyl) undecane-1-sulfonic acid (**1b**)*

Sodium 11-hydroxyundecane-1-sulfonate was synthesized as described previously [3]. An alternative purification, resulting in a product with less inorganic impurities, is the following: the product was dissolved in hot water, allowed to stand overnight at 5 °C and the resulting product slush filtered off at 5 °C followed by washing with cold water and freeze drying. The aqueous phase was concentrated using a rotary evaporator in order to collect some more product in the same procedure. ^{1}H NMR (D_2O): $\delta = 3.75$ (*t*, 2.1 H, –CH$_2$–O), 3.0 (*t*, 1.9 H, –CH$_2$–S), 1.9 (*t*, 2,0 H, –CH$_2$–C–S), 1.6 (*t*, 2.6 H, –CH$_2$–C–O), 1.4 (*m*, 15 H, (–CH$_2$–)$_7$). The spectrum showed no impurities. Elemental analysis: found (calculated $C_{11}H_{23}O_4SNa$): S 11.49 (11.69), Na 8.45 (8.38).

Sodium 11-hydroxyundecane-1-sulfonate (4.8 g, 0.018 mol) was dissolved in methanol/water 1:1 (*v*:*v*), acidified with some Wofatit OK 80 sulfonic cation exchanger, mixed with (0.05 g, 0.7 mmol) of calcium hydroxide in order to remove traces of sulfate, filtered and changed into the acid on a Wofatit OK-80 column. After freeze drying, the acid (4.35 g, 0.017 mol) was dispersed in dry dioxane, 50 ml, and freshly prepared **1a** (4 g, containing at least 0.02 mol **1a**) added. The suspension was stirred for 2 h at 30 °C, 2 h at 50 °C and then overnight at 30 °C. The mixture was filtered, the solid product suspended in 50 ml of water with sodium bicarbonate, 5 g. The product slush was centrifuged and washed with water, freeze dried, dissolved at 65 °C in *n*-propanol/water, precipitated with cold acetone at 5 °C, filtered and dried. Yield: 1.7 g (32%). ^{1}H-NMR (D_2O/pyridin-d^5 1:1, 60 °C): $\delta = 4.35$ (*t*, 2.0 H, –CH$_2$–O), 4.15 (*s*, 1.7 H, N–CH$_2$–CO), 3.15 (*t*, 1.7 H –CH$_2$–S), 2.05 (*m*, 1.8 H, –CH$_2$–C–S), 1.7 (*m*, 2.5 H, –CH$_2$–CO), 1.4 (*m*, 16.8 H, (–CH$_2$–)$_7$). Elemental analysis: found (calculated $C_{13}H_{27}NO_5S$): C 49.40 (50.63), H 8.02 (8.50), N 4.68 (4.54), S 10.37 (10.40), Na 0.75 (0). The latter result shows that the product is present partially as inner salt and partially as sodium salt (this also explains the low C and H values).

Sodium 11-(2-aminoethanoyl) undecane-1-sulfonate immobilized on silica (1)

1b (1.7 g, 5.4 mmol) was mixed with 3-(triethoxysilyl) propyl isocyanate (1.5 ml, 6 mmol) in 2.5 ml of dry triethylamine and refluxed for 50 h. After the reaction, the volatile part was evaporated at 100 °C/1 Torr. Yield: 1.65 g. The expected urea linkages could be observed with IR: 1550 and 1650 cm^{-1}. The product showed further peaks at: 2970 cm^{-1} (–CH$_3$), 2850 and 2930 cm^{-1}(–CH$_2$–), 2500 and 2700 cm^{-1} ($HNEt_3^+$), 1750 cm^{-1} (C=O in ester), 1450 cm^{-1}(–CH$_2$–), 1190, 1079, 1038 cm^{-1} (vs, SiO, SO_3^-, –OC–), 780 cm^{-1}, 550 cm^{-1}.

^{1}H-NMR: (DMSO): $\delta = 9.2$ (broad, H–N–), 6.2 (broad, 2.0 H, –NH–CO–NH–), 4.0 (*t*, 2.5 H, CO–O–CH$_2$–), 3.8 (*q*, 8.2 H, Si–O–CH$_2$–), 3.4 (*m*, 1.96 H, N–CH$_2$–CO), 3.05 (*m*, 8.2 H, HN–(CH$_2$–C)$_3$), 1.5–1.1 (*m*, 49.8 H, N–C–CH$_3$, Si–O–C–CH$_3$, C–CH$_2$–C), 0.5 (*m*, 2.9 H, Si–CH$_2$–). The activated **1b** was used without further purification.

Silica, 1.5 g, was mixed with 1.6 g (2.8 mmol) of activated **1b**, 10 ml of dry benzene/dioxane 1:4 (*v*:*v*) added, and refluxed for 1 h. The solvent was decanted from the solid phase, new benzene/dioxane was added and the mixture was stirred slowly overnight. Refluxing and decanting were repeated twice. In the solvent collected, about 2 mmol of ethanol was detected by gas chromatography. The solid product was washed with acetone, water, a dilute sodium sulfate solution in order to exchange triethylammonium salt groups, water and acetone, and dried at 60 °C. Yield: 1.73 g. Elemental analysis: C 11.06, H 2.53, N 1.81, S 1.41. Surfactant load calculated from S: 0.43 mmol surfactant/g.

4-Aminobutanoyl chloride hydrochloride (2a)

2a was prepared analogously to **1a**. The reaction was carried out starting with 4-aminobutanoic acid at 0 °C in acetyl chloride. The amino acid was added in two parts within 10 min. After 30 min, the ice bath was removed and the mixture stirred for another 30 min. The temperature needs some attentiveness, as the reaction may cause a sudden rise in temperature; above 40 °C, the product starts to oligomerize. Yield after washing at 0 °C with ether: 6.85 g (91%).

*$E_{12}C_{12}$ ester of 4-aminobutanoic acid (**2b**)*

In a two-necked reaction flask, $E_{12}C_{12}$ (20 ml, ~29 mmol), dried for 2 h at 60 °C/1 Torr on a rotary evaporator with a liquid nitrogen cold trap, was mixed with 15 ml of dry dichloromethane at 0 °C. In four parts, **2a** (6.8 g, 43 mmol) was added within 60 min. The milky dispersion was stirred for 3 h at 5–10 °C. Regularly, the HCl was removed by setting a slight vacuum. The extent of reaction was monitored by TLC (methanol/chloroform 1:3 (*v*:*v*)): the $E_{12}C_{12}$ peak did not disappear completely and a small peak of presumably linear oligomers of **2a** could be indicated with ninhydrin.

The product was filtered from its excess of insoluble **2a** and dried on a rotary evaporator provided with a cold trap at 40 °C/1 Torr. An almost colorless liquid remained, which became solid at room temperature. 6.5 g of it was purified by flash-chromatography with methanol/chloroform 1:5 (*v*:*v*). Thus, 3.8 g (58%) was obtained in pure form. ^{1}H-NMR ($CDCl_3$): $\delta = 4.2$ (*t*, 1.7 H, CO–O–CH_2–), 3.6 (*m*, 55.5 H, O–CH_2–CH_2–O), 3.5 (*t*, integral together with the 3.6-peak, O–CH_2–C–), 3.05 (*t*, 1.8 H, CH_2–NH_3^+), 2.5 (*t*, 1.8 H, CH_2–CO–O–), 2.05 (*m*, 2.0 H, N–C–CH_2–C–CO), 1,5 (*m*, 2.1 H, O–C–CH_2–C), 1.2 (*m*, 23.3 H, C–CH_2–C), 0.9 (*t*, 3.0 H, C–CH_3). Elemental analysis: found (calculated $C_{40}H_{82}NO_{14}Cl$): C 55.46 (57.43), H 9.38 (9.88), N 1.76 (1.67). The deviation in C must be seen in light of the uncertainty of the oligoethylene oxide chain length. From NMR and elemental analysis, the possibility of a small fraction of initial product $E_{12}C_{12}$ cannot be excluded.

***2b** immobilized on silica 100 (2)*

Activation of the surfactant was carried out by mixing **2b** (2.4 g, ~3.0 mmol) with triethylamine, 0.89 ml (6.4 mmol) and 3-(triethoxysilyl) propyl isocyanate (0.7 g, 3.05 mmol) in 50 ml of dry THF and stirring the mixture for 48 h, followed by refluxing for 2 h. The product was filtered and the solvents evaporated at 60 °C/down to 1 Torr. Yield: 3.1 g of a product which was not further purified.

In 2.9 g of activated amphiphile, 1 g of dry silica 100 was dispersed and allowed to stand overnight. In order to remove the ethanol originating in the reaction, 15 ml of dry toluene was added and then removed over 6 h at 60 °C on a rotary evaporator (toluene and ethanol form an azeotrope). During this procedure, new toluene was added three times. The product was then washed with toluene, dioxane, ether, and dried. Yield: 1.22 g. Elemental analysis: found C 13.17, H 2.91, N 0.91. Surfactant load according to C: 0.29 mmol/g. According to N: 0.33 mmol/g.

SDS adsorbed to alumina (3) [7]

2 g of alumina (elemental analysis: C 0.17, H 0.76, no S) was brought at a pH of 4.5 with dilute acetic acid-sodium acetate buffer in 30 ml of water, and SDS (500 mg, 1.7 mmol) was added. The mixture was shaken regularly. After 2 weeks the pH was 6.0. In order to remove an excess of unbound SDS, the product was washed with water of pH ~ 5 until too little SDS desorbed to solubilize the hydrophobic dye 1-(2-pyridylazo)-naphtol [17] in the washing water, washed with acetone and dried at 60 °C. Yield: 2.18 g. Elemental analysis: C 4.12, H 1.23, S 0.75. Tenside load according to S: 0.23 mmol/g. According to C: 0.27 mmol/g.

Hexadecyltrialkylammonium ions bound to a silica ion exchanger (4)

A sulfonic ion exchanger on silica base was synthesized according to [18]. Such an ion exchanger contains silica-bound 4-(3-silylpropyl-1-oxy) benzenesulfonic acid) groups covalently linked to the silica surface. Elemental analysis: C 6.84, H 1.79, N 0.08, S 2.24. The content of sulfonate groups was therefore 0.70 mmol/g. Loading with ethyldimethylhexadecylammonium bromide was carried out by stirring 1 g of ion exchanger with 0.5 g of surfactant in 10 ml of water, replacing the surfactant solution two times and washing the solid until no micelles and bromide were left in the washing water. Elemental analysis: C 19.21, H 3.34, N 0.92, S 1.79. Calculated tenside load from N and C (mean value): 0.63 mmol/g.

Results

Synthesis

We synthesized surfactants covalently immobilized at silica surfaces to avoid surfactant leaching, and tested them in catalytic hydrogenation. We compared these silicas in their effect on the reaction with SDS adsorbed to alumina and with a silica ion exchanger loaded with surfactant counterions.

The surfactants may be found on the solid surfaces as shown in an idealized manner in Fig. 1. The synthesis of the covalently immobilized tensides is presented in Fig. 2.

Esterification with amino acids gives the opportunity to easily introduce amino groups in surfactants. This way of introducing an amino group into polyethylene glycol (PEG) derivatives was not described before. However, a disadvantage of the $E_{12}C_{12}$-aminoacid ester is the presence of a sensitive ester bond, which, for example, did not support chromatography on silica overnight with chloroform/methanol, possibly due to transesterification with the eluent.

Some alternative reactions, noted in the literature to provide PEG derivatives with amino groups, were tried as well. However, along these pathways it appeared impossible to synthesize amino containing polyethyleneoxide monoalkyl ether (EyCx) varieties without chromatographic purification being necessary. Besides, the yields mentioned in the literature were not verified. The introduction of an amino group by etherification of $E_{12}C_{12}$-tosylate with potassium aminoethanolate or -cysteaminate [19] only resulted in very few, colored products. We also researched the tosyl substitution in $E_{12}C_{12}$-tosylate by azide in DMA at 100 °C, followed by hydrogenation of the azide group on Pd/C in ethanol at normal pressure [20]. Between the steps, the intermediates were purified after dissolution in methylene chloride by washing with aqueous sodium chloride. The product was purified chromatographically with chloroform/methanol 1 : 1 using 10 g silica/g product. This led to an amine-containing surfactant without ester bond in 32% yield. Despite the low yield (due to the hydrogenation step), this might be a good alternative for esterification.

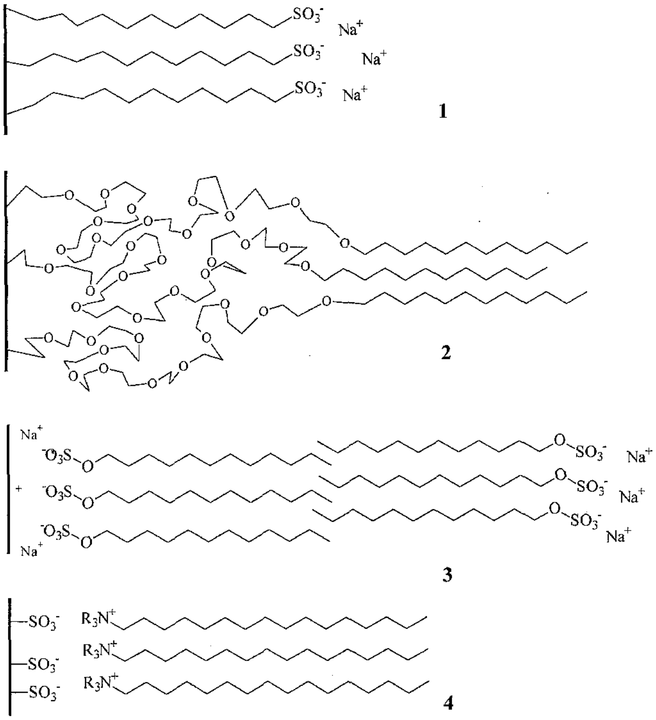


Fig. 1 Speculative picture of surfactants bound to solid surfaces in water

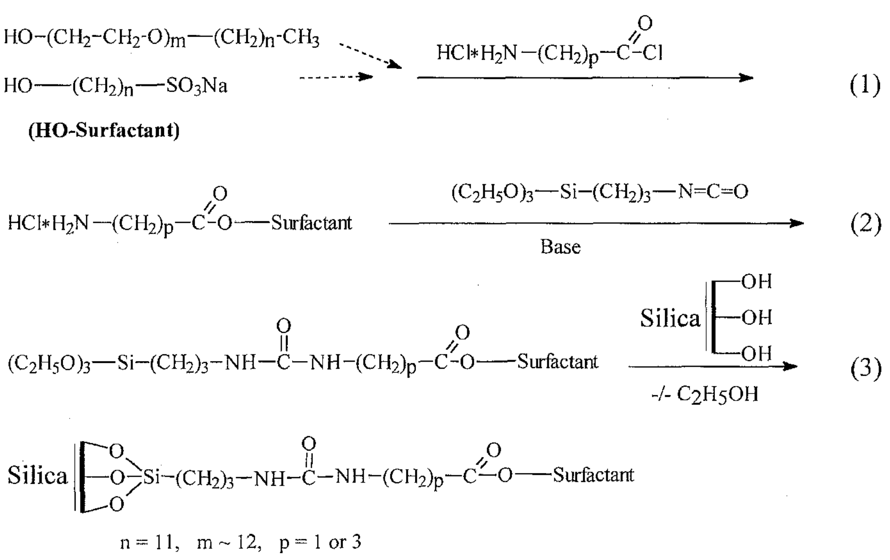
The amino acid chloride method was chosen to provide the ionic surfactant sodium 11-hydroxyundecane-1-sulfonate with an amino group, and gave good results, also due to the easy purification of the hardly soluble product.

It was possible to link the amino group containing surfactants to silica under mild conditions with 3-(ethoxysilyl) propyl isocyanate.

Inner surfaces of the surfactant systems

Some of the materials synthesized were characterized on their internal surfaces by determination of the BET isotherm. The surface of the starting material silica 100 was 300 m^2/g. The surface of **1** was 203 m^2/g, of **2** 174 m^2/g. The extent of areal decrease on “filling” the pores with surfactant seems normal: the amounts of tenside adhered

Fig. 2 Covalent immobilization of surfactants onto silica



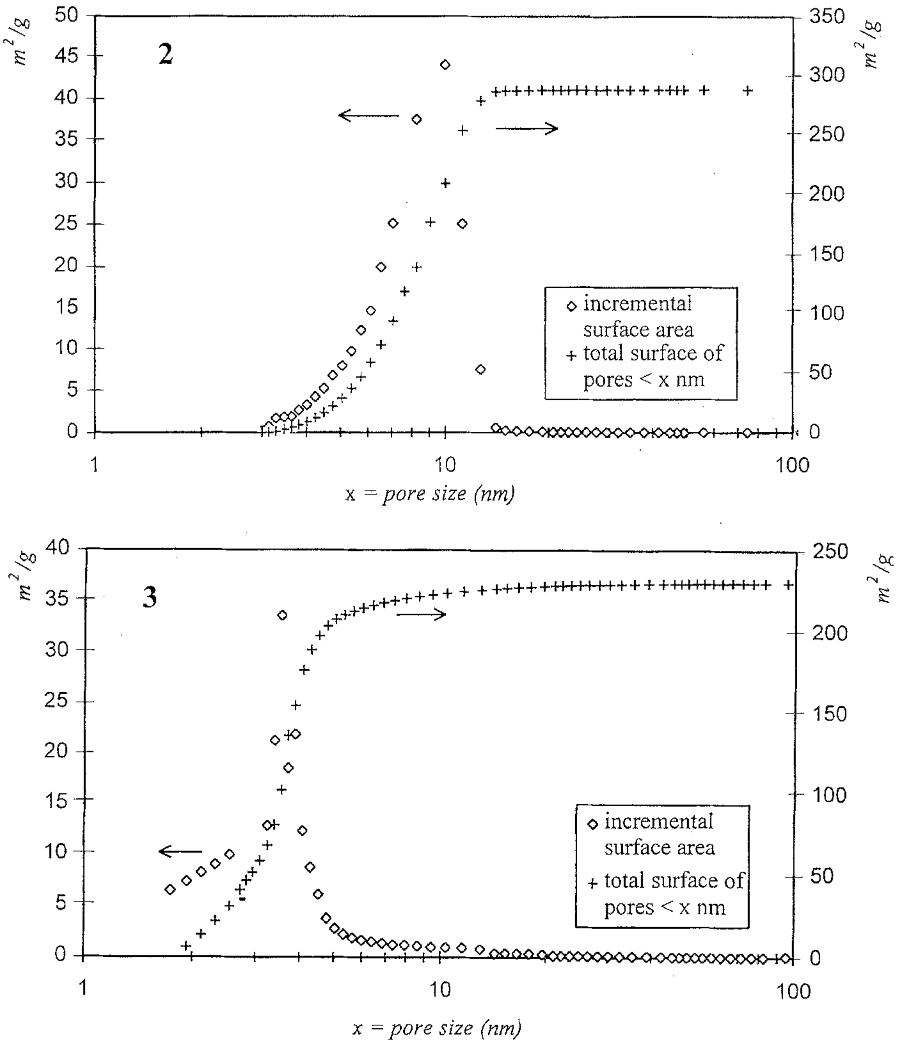


Fig. 3 Internal surfaces of the surfactant systems **2** (silica 100 containing ca. 30 wt% of dodecaethyleneglycol dodecylether covalently bound) and **3** (alumina containing ca. 7 wt% of adsorbed SDS). Both solid phases show a large internal surface area despite the bound surfactant layer, and a relatively narrow pore size distribution

to the silica are 180 and 250 mg surfactant/g coated silica in **1** and **2**, respectively. We are convinced, that the reactions do not block pores or destruct the channel structure of the support.

Surfactant system **3** showed an internal surface of 176 m^2/g: the surface of the starting alumina is not known. The pore size distributions of **2** and **3** are given in Fig. 3. In both materials a relatively small distribution of the pore sizes is observed, the pores of **3** being smaller than those of **2**. The manufacturer of the silica 100 indicates an average pore size of 10 nm. Interestingly, in **2** the pore size is still near this value despite its high surfactant content.

Use in asymmetric hydrogenation

The hydrogenation results are described in Table 1. Blank experiments were conducted either in water without amphiphiles (table entry 1) or in the presence of a nonamphiphilized ion exchanger (entry 9), which both led to a low reactivity and enantioselectivity. From the results, it is clear that normal, soluble surfactants induce a large improvement in the rate and selectivity of the reaction (entry 3–5). The surfactant concentrations were 13.3 mM (with surfactant: Rh = 20:1 mol/mol) or 33.3 mM (ratio 50:1), which is above the CMC of SDS (8 mM) and $E_{12}C_{12}$ (0.14 mM). Our intermediate HO–$(CH_2)_{11}$–SO_3Na foams in aqueous solution, but according to dye solubilization no micelles are formed up to 40 mM concentration. Indeed, this agent shows only a small effect on the reaction up to a 33.3 mM surfactant concentration (entry 2).

From the results with the insoluble systems, it may be concluded that the immobilized $E_{12}C_{12}$ in **2** forms an amphiphilic environment which makes the catalytic complex more active in water (entry 7). The experiment using a non-amphiphilised system with a large surface, i.e., the silica cation exchanger with sodium counterions of entry 9, showed that the enantioselectivity in the absence of an amphiphilic layer is lower. So the improved e.e. and half-times obtained must be caused by the special amphiphilic geometry of **2**.

The micellar effect of the immobilized sulfonic surfactant **1** is less clear (entry 6). This might be due to a surface which is not entirely filled out with surfactant molecules, as the tenside load is only 0.43 mmol/g, meanwhile the ionic exchanger **4** contains 0.63 mmol/g of surfactant. This lower load may cause "gaps" between the hydrophobic chains filled with water, especially because the hydrophobic chains have no spacer group as in **2**, and therefore have less opportunity to assemble.

The silica ion exchanger **4** is also effective in hydrogenation (entry 10). We suppose that in **4** the bound surfactant molecules are able to move and associate following the hydrophobic effect, because they are solubilized in water as counterions. From our results, we conclude that the systems in which the hydrophobic chains can move, like **2** and **4**, are the best regarding their hydrogenation properties.

That the half-times are longer with the heterogenized systems than with dissolved SDS, might be due to diffusion limitation. This may also explain the slower hydrogenation on **2** as compared to the other heterogeneous systems. In **2**, the micropores of the silica must be partially filled up by the bulky oligomer molecules: the silica, having a porosity of 1.3 ccm/g according to the manufacturer, is loaded to about 30% of its weight with organic material.

Table 1 Hydrogenation of 1 mmol of methyl (*Z*)-α-acetamidocinnamate in 15 ml of water with 0.01 mmol $[Rh(COD)_2]BF_4$ and 0.011 mmol BPPM with H_2 at normal pressure and 25 °C. Effect of various surfactant systems

Entry	Amphiphile (see also Fig. 1)	Amphiphile: Rh mol/mol	Optical yield % e.e. *R*	$t_{1/2}$ min
1	pure water	00:1	78	~90
2	$HO–C_{11}–SO_3Na$	50:1	83	45
3	$C_{12}–SO_4Na$ (SDS)	50:1	94	3.5
4	$C_{12}–SO_4Na$ (SDS)	20:1	94	6
5	$HO–(C_2–O)_{12}–C_{12}$	20:1	95	5
Silica-bound surfactant				
6	**1**	20:1	78	17
7	**2**	20:1	93	24
Alumina-adsorbed SDS				
8	**3**	20:1	90	7.5
Silica exchanger				
9	without amphiphile	20:1 (SO_3^-:Rh)	70	40
10	**4**	20:1	92	11

Approximate surfactant densities at the solid phases: 1 0.43 mmol/g, 2 0.31 mmol/g, 3 0.25 mmol/g, 4 0.63 mmol/g.

Probably the high activity of **3** is due to the favorable bilayer structure which may be proposed on its surface [4–7]. As system **3** has smaller pores than the silica systems **1** and **2**, one should expect a slower reaction. It may be concluded that for small surfactant molecules like SDS the pore size is not very critical.

Reuse of the systems

Some of the systems were reused by sedimentation, separation from the aqueous phase and provision with new water and substrate. The reuse experiments are shown in Table 2. The results show that all surfactant systems can be separated from the water phase with only unsignificant rhodium losses. From **4**, the rhodium content in the solid phase was not precisely determinable; the digestion solution became problematic, presumably by particles from the modified silica. However, because in 10 hydrogenation cycles no traces of rhodium were found in the aqueous phase, we suppose the rhodium leaching also to be insignificant in this system.

When after some hydrogenation cycles the reaction mixture with the silica was extracted as a whole with chloroform instead of filtering off the surfactant system, a rise of the e.e. value was observed. We explain this by favored entrapment of the *R* enantiomer into the surfactant, leading to an enrichment of *R* in the solid phase. The product, which is soluble in chloroform, might thus be recovered on extraction. This enrichment of insoluble product in the solid phase might also be the cause of the poorer reuseability of **2**.

Table 2 Repeated hydrogenation with the same rhodium containing surfactant systems after separation of the catalytic solid phase from the products and addition of new substrate

Amphiphile	Cycle	e.e. % *R*	$t_{1/2}$ min	Phodiumin solid phase found wt.%	calculated
1	1	78	17	traces in aqueous phase	
	6	74	7	0.21	0.22
2	1	93	24		
	2[a)]	96	62	traces in aqueous phase	
				0.13	0.14
3	1	90	7.5	0.10	0.12
4	1	92	11	0.15[b)]	0.30
	2	91	12	no traces in aqueous phase	
	9	84	24.5	no traces in aqueous phase	
	10[a)]	94	48	0.08[b)]	030

[a)] After this cycle, the surfactant system did not sedimentate sufficiently anymore – the aqueous phase was extracted with chloroform without prior separating of the rhodium containing solid phase.

[b)] the silica ion exchanger caused problems in the rhodium determination.

The very low rhodium leaching of **4** as compared to the other systems might be explained by the fact that the rhodium complex is positively charged, and that in the first hydrogenation an ion exchange might take place with some of the tenside molecules. Thus, the complex is not only entrapped but also ionically fixed onto the support. Interestingly, the rhodium is not even washed out of any system on extraction with chloroform, indicating that the micellar environment is very favorable for the complex.

Conclusion

It is possible to fix surfactants covalently or by ionic interaction onto silica (Fig. 1, type **1**, **2** and **4**). When the hydrophobic tails of the bound surfactants are free to move and assemble, they keep their amphiphilic character and form a kind of micellar layer, as indicated by their influence on a rhodium-catalyzed reaction in water. Useful for this reaction is also a simple system with adsorbed SDS on alumina (Fig. 1, type **3**). The small mean pore size of this system, about 4 nm, was not critical as was shown by the high activity of this system.

The rhodium complex is found almost entirely in the functionalized silica after hydrogenation, making multiple use of the surfactant system principally possible.

Acknowledgement Thanks are due to Mrs. B. Harzfeld, Mrs. M. Jäkel, Mrs. K. Kortus, Mrs. R. Kross and Mr. Dr. W. Baumann for analytical work, and especially to Mrs. L. Buths for carrying out the hydrogenations.

Surface characterizations were carried out by Viktor Skolnik at the Twente University, Enschede, the Netherlands. We are grateful for the help offered at this university.

The Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie are thanked for the financial support of this research.

References

1. Oehme G, Paetzold E, Selke R (1992) J Mol Catal 71:L1
2. Grassert I, Paetzold E, Oehme G (1993) Tetrahedron 49:6605
3. Flach HN, Grassert I, Oehme G (1994) Macromol Chem Phys 194:3289
4. Couzis A, Gulari E (1993) Langmuir 9:3414
5. Söderlind E (1994) Langmuir 10:1122
6. Söderlind E, Björling M, Stilbs P (1994) Langmuir 10:890
7. Yu CC, Wong DW, Lobban LL (1992) Langmuir 8:2582
8. Hartley FR (1987) In: Hartley FR (ed) The Chemistry of the Metal-Carbon Bond. Wiley & Sons Inc, Chichester, Chapter 14
9. Hong L, Ruckenstein E (1994) J Mol Catal 90:303
10. Neiva SMC, Santos JAV, Moreira JC, Gushikem Y, Vargas H, Franco DW (1993) Langmuir 9:2982
11. Tundo P, Venturelli P (1979) J Am Chem Soc 101:6606
12. Lavine BK, Hendayana S, Tetreault J (1994) Anal Chem 66:3458
13. Alandis N, Rico-Lattes I, Lattes A (1994) New J Chem 18:1147
14. Waddell WH, O'Haver JH, Evans LR, Harwell JH (1995) J Appl Polym Sci 55:1627
15. Fischer E (1905) Ber Dtsch Chem Ges 38:2914
16. Levine S (1954) J Am Chem Soc 76:1382
17. Furton KG, Norelus A (1993) J Chem Educ 70:254
18. Selke R, Čapka M (1990) J Mol Catal 63:319
19. Ziegast G, Pfannemüller B (1984) Markromol Chem Rapid Commun 5:363
20. Zalipsky S, Gilon C, Zilkha A (1983) Eur Polym J 19:117