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Enantioselective hydrogenation of itaconic acid and its derivates with sol-gel immobilized Rh/BPPM catalysts

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ARTICLE INFO

Article history: Received 27 February 2012 Received in revised form 25 June 2012 Accepted 16 October 2012 Available online 22 October 2012

Keywords: BPPM ligand Heterogeneous catalysis Hydrogenation Chloro(1,5-cyclooctadiene) rhodium (I) dimer Sol-gel process

ABSTRACT

Itaconic acid and some of its derivates were hydrogenated with sol-gel entrapped Rh/BPPM catalysts in methanol solutions. The immobilization process was carried out by different gel building agents: hydrophilic tetramethyl orthosilicate Si(OMe)₄ (TMOS) and tetraethyl orthosilicate Si(OEt)₄ (TEOS), hydrophobic triethoxyphenylsilane PhSi(OEt)₃/TMOS and trimethoxy(octyl)silane OcSi(OMe)₃/TMOS. The choice of the silane precursor influences the enantioselectivity and the rate of the reaction because of the hydrophobic interactions between catalyst, gel and substrate. The immobilized catalyst could be recovered and recycled several times under N₂-atmosphere. About 90–99% ee were achieved for the hydrogenation of itaconic acid to (S)-(+)-2-methyl succinic acid, and about 14% ee for the hydrogenation of dimethylitaconate to (S)-(+)-2-methyl-succinic acid dimethylester.

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1. Introduction

The entrapment of organic and organometallic compounds into sol gel matrices is an important technique for different applications, e.g. photochemistry, chemical sensing and optics [1], biochemistry and enzyme technology [2]. Furthermore, this technique allows for immobilization of homogeneous catalysts in order to overcome the major drawback of homogenous catalysis, the difficult separation of the products and the catalyst after the reaction. Catalysts entrapped in sol-gel matrices can be used in a variety of reactions: ligand-free Heck and Suzuki couplings of aromatic compounds with Pd(OAc)₂ catalyst [3,4], the RhCl₃·H₂O/Aliguat 336 catalyzed isomerization of hydrophobic allylarenes [5], hydroformylation of styrene derivates with [Rh(cod)Cl]₂ [6] and disproportionation of dihydroarenes with RhCl₃·H₂O/Aliquat 336 or Pd(OAc)₂ catalysts [7]. The replacement of organic solvents by aqueous solutions with different surfactants (aqueous-micellar solutions or microemulsions) allows the more environmentally friendly performance of different reactions [8].

In this contribution we investigate the enantioselective hydrogenation of itaconic acid and some of its derivates by Rh/BPPM catalysts entrapped within different sol-gel matrices (Scheme 1). The homogeneously catalyzed hydrogenations of itaconic acid with in situ generated Rh/BPPM catalyst in methanol and other organic solvents were already investigated by many research groups and high enantioselectivities and fast reaction rates were obtained [9–11].

Also the hydrogenation of itaconic acid in aqueous solutions and a mixture of aqueous-organic solvents [12] or the hydrogenation of (Z)-methyl- α -acetamidocinnamic acid in aqueous-micellar solutions [13,14] were investigated earlier. High enantioselectivities could be obtained for the hydrogenation of itaconic acid and its derivates in aqueous-micellar solution with different homogeneous rhodium catalysts [15,16]. Because of the use of surfactants or micelle forming agents, the catalysts could be recovered by micellar enhanced ultrafiltration as shown by Dwars et al. [17].

The immobilization of the in situ generated complexes within sol-gel materials allows a better and easier separation of these catalysts from solution and facilitates their reuse, which greatly improves the productivity of the catalyst. Different mesoporous silica materials can be used as support materials in order to adapt the catalyst to the substrate of the reaction [18–20].

The reactions are carried out in methanol as organic solvent and in aqueous solutions that contain surfactants to solubilize the hydrophobic reactants in water.

We study the influence of different parameters (temperature, reaction media, hydrophobicity of the substrate and support material, type of the surfactant and amount of the catalyst) on the reaction rate and enantioselectivity in order to derive a recipe for an optimal immobilized catalyst.

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^{1381-1169/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.molcata.2012.10.016



Scheme 1. Hydrogenation of itaconic acid (R = H), dimethyl ($R = CH_3$), diethyl ($R = C_2H_5$) and n-dibutyl ($R = C_4H_9$) itaconates.

2. Experimental

2.1. Chemicals

(2*S*,4*S*)-1-Tert-butoxycarbonyl-4-diphenylphosphino-2-(diphenylphosphinomethyl)pyrrolidine (BPPM), tetraethyl orthosilicate (TEOS), trimethoxyphenylsilane (PhSi(OMe)₃), triethoxy(octyl)silane (OcSi(OEt))₃, itaconic acid (IA), tetramethyl orthosilicate (TMOS), (trimethylsilyl)diazomethane solution, phosphorus and rhodium ICP standard solutions were obtained from Sigma–Aldrich company. Diethyl itaconate (DEI) stabilized with trichlorobenzene (TCB) and dibutyl itaconate (DBI) were acquired from TCI Europe. Dimethyl itaconate (DMI), chloro(1,5-cyclooctadiene) rhodium(I) dimer [Rh(cod)Cl]₂ and chloronorbornadiene rhodium(I) dimer [Rh(nbd)Cl]₂ were purchased from ABCR GmbH & Co., Karlsruhe, Germany.

The structures of catalysts and ligand are shown in Scheme 2.

2.2. Immobilization of the rhodium catalyst

The general procedure for the entrapment of the Rh/BPPM catalyst using different gel building agents is shown in Scheme 3. In every case, after preparation of the catalysts by the different procedures described below (a–c), the catalysts were dried for 24 h in a vacuum oven under a reduced pressure of 1000 Pa and a temperature of 30 °C, washed carefully 3 times with 10 mL boiling water and dried again. The washing liquids were analyzed for their rhodium and phosphorous content (catalyst leaching) with ICP-OES.

2.2.1. Hydrochloric acid catalyzed entrapment in hydrophilic gel

The two step entrapment of the catalyst was carried out under N₂ atmosphere using the procedure described by Gelman et al. [21]. A mixture of 2.50 mL TMOS (16.92 mmol) in 3.50 mL methanol and 0.78 mL hydrochloric acid (prepared from 0.1 mL of 1.1 N HCl and 9.9 mL H₂O) was stirred for 10 min at 25 °C. Separately the Rh/BPPM

catalyst was formed in situ from $10 \text{ mg} [\text{Rh}(\text{cod})\text{Cl}]_2 (0.022 \text{ mmol})$ and 20 mg BPPM (0.044 mmol) dissolved in 0.78 mL tetrahydro-furan.

The hydrolyzed TMOS solution was mixed with the activated catalyst and 0.83 mL ammonia solution (0.1 N) to catalyze the gelation process. The gelation occurred after 20–30 min.

The immobilization procedure using [Rh(nbd)Cl]₂ as precursor was the same. Because of lower solubility of this rhodium precursor in tetrahydrofuran, it was solubilized in 10 mL methanol.

2.2.2. Entrapment in hydrophilic support

The entrapment of the Rh/BPPM catalyst in the modified support could be realized with TEOS or a mixture of TMOS and TEOS under N₂-atmosphere. After the hydrolysis of 1.58 mL TEOS (9.88 mmol) in 5.6 mL ethanol and 0.4 mL of distilled water for 24 h, the solution was added to the catalyst solution (prepared similarly as described in Section 2.2.1). Then a small amount of conc. triethylamine (3–5 drops) was added to the mixture to catalyze the gelation process. The gelation of the catalyst occurred after about 24 h.

For the preparation of the mixed TMOS/TEOS immobilized catalyst, the hydrolyzed TMOS solution (3.6 mL TMOS (23.0 mmol), 2.4 mL methanol (94.8 mmol) and 2.0 mL water (111 mmol)) was added to the hydrolyzed TEOS solution.

2.2.3. Entrapment in hydrophobic gel

The procedure for the immobilization of the catalyst in hydrophobic supports is comparable to the immobilization of a palladium catalyst for the Heck Coupling reaction as shown by Rozin-Ben Baruch et al. [3]. A mixture of 2.1 mL octyl trimethoxy silane (9.88 mmol) or 1.61 mL phenyltriethoxysilane (6.68 mmol) was stirred for 24 h in 4.2 mL ethanol and 0.4 mL distilled water. Then the hydrolyzed tetramethoxy orthosilicate solution was added (Section 2.2.2) and stirred for 20 min. The combined solutions were mixed with Rh/BPPM in tetrahydrofuran (prepared similarly as described in Section 2.2.1) and the gelation was completed within 4–8 days.





Scheme 3. Entrapment of the Rh/BPPM catalyst with different gel building agents (PhTMOS or OcTMOS = hydrolyzed TMOS + PhSi(OEt)₃ or OcSi(OMe)₃ solution).

2.3. Hydrogenation procedure

The set up of the hydrogenation apparatus [22,23] is shown in Scheme 4. About 1.0–1.4 g of the yellow-orange sol gel immobilized catalyst, a desired amount of substrate and 95 mL of solvent (methanol, water or aqueous-micellar solution) were added to a stirred tank reactor and stirred at 400 rpm under N₂-atmosphere at the desired reaction temperature. The N₂ was replaced by H₂ $(p = 1.1 \times 10^5 \text{ Pa})$ without stirring and the reaction was started by turning the stirrer on 800 rpm again. The reactions were performed in semi-batch mode with hydrogen being permanently added to the stirred tank reactor to achieve a constant total pressure of 1.1×10^5 Pa in reactor. The cumulative hydrogen consumption and the pressure during the reaction were recorded using a Bronkhorst flow meter and pressure controller (Bronkhorst Mättig GmbH, Kamen, Germany), respectively (see Scheme 4). The sensitivity of measured hydrogen consumption was ± 0.4 mL. The pressure and the hydrogen flow during the reaction were registered and



Scheme 4. Hydrogenation set up (Pl, pressure indicator; PC, pressure controller; FM, flow meter; T, thermostat).

analyzed on a PC, from these results the substrate concentration $c_{\text{substrate}}$ and the conversion *X* were calculated.

A typical diagram of the experimental data obtained for the hydrogenation of itaconic acid with a homogeneous Rh/BPPM catalyst, is shown in Fig. 1.

After the reaction, the solution was analyzed by GC to determine the conversion and the selectivity and by ICP to check for catalyst leaching. For recycling experiments, the immobilized catalyst was left in the reactor under N_2 atmosphere after the reaction and reused directly again in several runs by adding new substrate.

2.4. Instruments

The separation of catalyst and silica support was carried out by microwave decomposition ($p = 20 \times 10^5$ Pa, t = 35 min and T = 200 °C) with a CEM Discover SP-D (sample preparation – digestion) instrument (CEM GmbH, Camp-Lintfort, Germany). Before this procedure, the catalysts were ball milled, and then mixed with 12 mL of an HNO₃/HCl/H₂SO₄ solution (ratio: 2eq/6eq/4eq). After the microwave treatment, the white solid silica was removed by filtration and the solution of detached catalyst was analyzed for rhodium and phosphorus content using a Varian 715-ES Optical Emission Spectrometer (ICP-OES). Calibration of the instrument was performed with commercial rhodium and phosphorus standards.

The reaction conversion and the enantiomeric excess of the hydrogenation of DMI were obtained by gas chromatography using a Hewlett–Packard model HP 5710 equipped with a Lipodex E column (Macherey-Nagel GmbH & Co. KG, Düren, Germany). The following conditions were used for the analysis: $T_{injector} = 200 \,^{\circ}C$, $T_{detector} = 250 \,^{\circ}C$, $T_{oven} = 80 \,^{\circ}C$ and $p_{column} = 60 \times 10^3 \,\text{Pa}$, carrier gas = N₂. For itaconic acid, before analysis the sample was treated with (trimethylsilyl) diazomethane and then analyzed the same way as described for DMI. For DEI and DBI, the conversion was calculated from the GC results.

 N_2 -BET specific surface area measurements of sol-gel immobilized rhodium catalysts were obtained by a Micromeritics Gemini 1325 instrument. Transmission electron microscopy was performed with a conventional LaB₆-TEM Tecnai G220 S-TWIN



Fig. 1. Reaction profiles for the homogeneous hydrogenation of itaconic acid in methanol: (a) cumulative hydrogen consumption V_{H_2} and hydrogen flow (dV/dt); (b) conversion *X* and substrate concentration c_{IA} . *Reaction conditions*: 15.4 mmol substrate, 0.022 mmol [Rh(cod)CI]₂, 0.044 mmol BPPM, 100 mL solvent, 1.1×10^5 Pa H₂, 800 rpm, 30 °C.

instrument (FEI Company, USA) operated at 200 kV and equipped with EDAX-EDS for identification of elemental compositions.

3. Results and discussion

3.1. Catalyst preparation and characterization

The heterogeneously catalyzed hydrogenations of itaconic acid and derivates were realized with sol gel immobilized and in situ generated Rh/BPPM catalysts. The catalyst complex was obtained by ligand exchange of cyclooctadiene (cod) or norbornadiene (nbd) ligand in rhodium precursors by the enantioselective pyrrolidine ligand BPPM. The use of the rhodium precursor containing norbornadiene ligand is preferred in hydrogenation reactions because of a faster ligand exchange rate [24,25].

The catalysts were prepared as described in Section 2 and after successful entrapment of the rhodium into the silica matrix, the support changes its color from white to yellow (see Fig. S1 and Fig. S2 in supporting information). After the synthesis, the washing liquids were analyzed by ICP-OES and the contents of phosphorus and rhodium were determined to be <0.02 mg rhodium (0.5% leaching) and <0.02 mg phosphorus (1.5% leaching) in 10 mL of water, respectively.

The loading of the heterogeneous catalysts were about 2-3 wt% Rh/BPPM, with 0.1-0.2 wt% rhodium and the average particle size was 200–500 μ m. The specific surface areas of the catalyst and the

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Specific surface area A of immobilized Rh/BPPM catalysts and support materials.

	A (m ² /g)
TMOS-derived silica	397
TEOS-derived silica	467
Rh/BPPM@TMOS-derived silica	383
Rh/BPPM@TEOS-derived silica	225
Rh/BPPM@PhTMOS-derived silica	327
Rh/BPPM@OcTMOS-derived silica	327

support materials were obtained from BET measurements and the results are given in Table 1.

After immobilization of the Rh/BPPM catalyst, the specific surface area decreases slightly from $397 \text{ m}^2/\text{g}$ to $383 \text{ m}^2/\text{g}$, if TMOS-derived silica is used and to 327 m²/g, if PhTMOS- or OcTMOS-derived silica's are used. For TEOS-derived silica we observed a stronger decrease in the specific surface area. A reason for the decreased specific surface area could be a blocking of the smaller pores in the support material by the immobilized catalysts. The average pore sizes of the catalysts were between 2.1 and 3.2 nm [5,7,26]. The TEM images of tetramethyl orthosilicate immobilized rhodium catalyst showed in Fig. 2a indicate that the catalysts used in the hydrogenation reaction of itaconic acid and derivates are highly porous. Their average pore size is 1-2 nm and the metal complexes are intercalated in the pore walls of the support material, but cannot be indicated in Fig. 2a because of low loading of the support with rhodium. However the energy dispersive X-ray spectroscopy measurement EDX (Fig. 2b) showed small amounts of metallic rhodium nanoparticles and large amounts of SiO₂ support in this sample.

3.2. Homogeneous vs. heterogeneous hydrogenation reaction

The hydrogenation of itaconic acid was carried out with a homogeneously dissolved Rh/BPPM catalyst and with an immobilized Rh/BPPM catalyst on TMOS derived silica. The reaction rate for the sol-gel immobilized Rh/BPPM catalyst is slower than for the homogeneous catalyst in methanol (Fig. 3), but the same enantiomeric excess is obtained (ee = 90–97%). The turnover frequency (TOF) for Rh/BPPM catalyst on TMOS derived silica was ~2400 h⁻¹ and about 3 times lower than for the homogeneous catalyst (TOF ~ 6100/h), because the reaction rate can be influenced by mass-transport limitations within the heterogeneous sol-gel material or a decrease in activity of the catalyst due to its encapsulation inside the silica material.

3.3. Temperature dependence of the hydrogenation reaction

To check for mass transport limitation, the temperature dependence of the hydrogenation reaction was studied (Fig. 4). The reaction rate increases with increasing temperature as expected. From the slope of the regression line in the Arrhenius plot, the activation energy E_A of the chemical reaction was calculated (Table 2).

For the hydrogenation of itaconic acid in methanol solution the reaction rate is higher in water due to the higher solubility of hydrogen in methanol. Also the hydrogenation reaction using the catalyst with 1:2 [Rh(cod)Cl]₂:BPPM molar ratio is much faster than with 1:4 molar ratio. The activation energies E_A of the hydrogenation with heterogeneous catalyst in methanol and also in water or aqueous-micellar solutions (Table 2) is comparable with the activation energies when using a homogeneous catalyst (1 Rh(cod)SO₃CF₃:2BPPM) [22]. That means that the heterogeneously catalyzed hydrogenation is not mass transport limited and the decrease of the reaction rate can be explained by the part deactivation of the catalyst or encapsulation in silica material. An influence of pore diffusion on the reaction rate would be I. Volovych et al. / Journal of Molecular Catalysis A: Chemical 366 (2013) 359-367



Fig. 2. (a) TEM image and (b) EDX spectra of typical TMOS based supported Rh/BPPM catalyst after the hydrogenation of itaconic acid in methanol.

indicated by a strong decrease E_A . Also the variation of stirring rates between 600 and 1200 rpm in homogeneous and heterogeneous reactions shows no increase of reaction rate with increasing stirring intensity. That means the hydrogenation is not limited through the transport between the gas and the liquid phase. Only

the reactions with stirring rates below 600 rpm are transport limited.

All following hydrogenation reactions were realized at 30 $^{\circ}$ C, were the reaction proceeds with a reasonable rate, due to good catalyst activity and H₂ solubility.

Table 2

The activation energies for the hydrogenation of itaconic acid.

[Rh(cod)Cl] ₂ :ligand ratio	Solvent	E _{A, heterogeneous} (kJ/mol)	ee _{heterogeneous} (%)	E _{A,homogeneous} ^a (kJ/mol)	ee _{homogeneous} ^b (%)
1:4	Methanol	33.4	98		
1:2	Methanol	50.5	98	49.9	95
1:4	Water	24.4	37	33 ^c	38 ^c

^a Rh(cod)₂SO₃CF₃/BPPM [22].

^b [Rh(cod)Cl]₂/BPPM.

c H₂O/SDS.



Fig. 3. Comparison between homogeneous and heterogeneous hydrogenation of itaconic acid. *Reaction conditions*: 15.4 mmol substrate, 0.022 mmol [Rh(cod)Cl]₂, 0.044 mmol BPPM, 100 mL methanol, 1.1×10^5 Pa H₂, 800 rpm, 30 °C.

3.4. Substrate variation

The enantioselective Rh/BPPM@TMOS-gel catalyzed hydrogenation reaction can be performed with different itaconic acid derivates. The cumulative hydrogen consumption for the hydrogenation of IA, DMI, DEI and DBI is shown in Fig. 5. For IA, the reaction is very fast and full conversion is achieved within 25 min. For DMI and DEI, full conversion is achieved only within 50–80 min, but interestingly, the reaction with DEI is faster than with DMI. For DBI, the conversion after 70 min is only 70%. From these results it is clear that the conversion of the reaction increases with decreasing



Fig. 4. Arrhenius plots of the hydrogenation of itaconic acid in water and methanol at 1:2 and 1:4 Rh:BPPM ratio. *Reaction conditions*: 15.4 mmol substrate, 0.022 mmol [Rh(cod)Cl]₂, 0.044 mmol BPPM, 100 mL solvent, 1.1×10^5 Pa H₂, 800 rpm.



Fig. 5. Substrate variation in the hydrogenation with Rh/BPPM on TMOS-derived silica in methanol: itaconic acid (IA), dimethyl itaconate (DMI), diethyl itaconate (DEI), dibutyl itaconate (DBI). *Reaction conditions*: 15.4 mmol substrate, 0.022 mmol [Rh(cod)Cl]₂, 0.044 mmol BPPM, 100 mL solvent, 1.1×10^5 Pa H₂, 800 rpm, 30°C.

hydrophobicity of the substrates (decreasing C-chain length). The comparison to the same reactions with a homogeneous catalyst also shows that the difference is caused by the reactivity of the substrates. In order to examine the influence of the interactions between the reactant and the catalyst support material a surface modification with hydrophobic functional groups is introduced in the next section.

3.5. Influence of the support materials

Besides the hydrophobic character of the substrate, the polarity of the catalyst surface also influences the rate of the hydrogenation reaction. The catalysts were prepared with different hydrophilic and hydrophobic sol gel building agents: tetramethyl orthosilicate (TMOS), tetraethyl orthosilicate (TEOS), hydrophobically modified TMOS (Ph/TMOS and Oc/TMOS). The specific surface areas for the immobilized catalysts and support materials are shown in Table 1. The specific surface areas of the different support materials, except for TMOS, are about $350 \text{ m}^2/\text{g}$.

The hydrogenations of IA, DMI and DBI were carried out with sol-gel supported Rh/BPPM catalysts with these different hydrophobic surface modifications and the reaction profiles are shown in Fig. 6.

The reaction rate with more hydrophilic substrates (IA, DMI) increases if the hydrophilic surfaces are used (TMOS, TEOS). The reaction rate was quite the same in the hydrogenation of more hydrophobic DBI with the catalyst with hydrophobic support. The use of Rh/BPPM catalyst immobilized in hydrophobically modified silica is preferred in reactions with more hydrophobic substrates for example DBI because of hydrophobic interaction between the



Fig. 6. Cumulative hydrogen volume for the hydrogenation of (a) itaconic acid, (b) dimethylitaconate, (c) dibutylitaconate in methanol with Rh/BPPM catalyst@ different support materials. *Reaction conditions*: 15.4 mmol substrate, 0.022 mmol [Rh(cod)Cl]₂, 0.044 mmol BPPM, 100 mL methanol, 1.1×10^5 Pa H₂, 800 rpm, 30°C.

substrate and the catalyst surface. The same effect was seen in a Heck reaction with $Pd(OAc)_2$ and aromatic substrates [3]. The advantages of the hydrophobically modified surfaces were already shown in literature; the catalysts formed on these surfaces are more stable (no leaching into the solution) because of more branched pore structure [2].

3.6. Use of different reaction media

Most homogeneously catalyzed reactions are carried out in conventional organic solvents, but the use of water as solvent allows more environmentally friendly processes. The main problem using water, as reaction medium is that many substrates are hydrophobic and cannot be solubilized completely in water. The addition of surfactants with concentrations higher than the critical micelle concentration (cmc) results in the formation of micelles able to solubilize the substrates, depending on the partition coefficient, in their cores (hydrophobic) or in the palisade layer (hydrophilic) [27]. By increasing the surfactant concentration to higher amounts, the solubility of the substrate can be improved. In Fig. 7a the reaction profiles for the hydrogenation of itaconic acid in methanol, water and in aqueous-micellar solutions of different surfactants are shown. As expected, because of the higher solubility of hydrogen (4-5 times higher), the reaction is faster in methanol than in the aqueous media, but the influence of the surfactant on the hydrogenation rate of this hydrophilic substrate is low. In the aqueous-micellar solutions the hydrogenation reactions proceed with a similar rate as in water, because of the high solubility of itaconic acid in water (ca. 40 g/L). For the solubilization and hydrogenation of IA the surfactant is not required. For the hydrogenation of DMI, the use of more hydrophobic nonionic



Fig. 7. Cumulative hydrogen volume for the hydrogenation of (a) itaconic acid and (b) dimethyl itaconate in methanol, water and aqueous-micellar solutions. *Reaction conditions*: 15.4 mmol substrate, 0.022 mmol [Rh(cod)Cl]₂, 0.044 mmol BPPM, 100 mL solvent, 1.1×10^5 Pa H₂, 800 rpm, 30 °C.

Table 3

Conversions, enantiomeric excess (ee) and turnover frequencies (TOF) for hydrogenation reactions in methanol and in aqueous-micellar solutions with homogeneous and TMOS supported Rh/BPPM catalysts, respectively.^a

Entry	Catalyst	Substrate	X (%) ^c	ee (%) ^c	$TOF (1/h)^b$	Support	Solvent
1	[Rh(cod)Cl] ₂	IA	100	99	6132	_	Methanol
2	[Rh(cod)Cl] ₂	IA	100	98	2390	SiO ₂	Methanol
3	[Rh(nbd)Cl] ₂	IA	100	99	3947	-	Methanol
4	[Rh(nbd)Cl] ₂	IA	100	98	4426	SiO ₂	Methanol
5	[Rh(cod)Cl] ₂	IA	25	37	126	SiO ₂	Water
6	[Rh(cod)Cl] ₂	IA	44	35	201	SiO ₂	H ₂ O/methanol
7	[Rh(cod)Cl] ₂	IA	100	2	111	SiO ₂	H ₂ O/SDS ^d
8	[Rh(cod)Cl] ₂	IA	100	95	377	-	H ₂ O/CTAB ^e
9	[Rh(cod)Cl] ₂	IA	100	23	163	SiO ₂	H ₂ O/CTAB ^e
10	[Rh(cod)Cl] ₂	IA	100	88	565	-	H ₂ O/TX-100 ^d
11	[Rh(cod)Cl] ₂	IA	45	30	195	SiO ₂	H ₂ O/TX-100 ^d
12	[Rh(cod)Cl] ₂	IA	100	2	251	SiO ₂	Microemulsion ^f
13	[Rh(cod)Cl] ₂	DMI	100	61	592	-	Methanol
14	[Rh(cod)Cl] ₂	DMI	56	12	398	SiO ₂	Methanol
15	[Rh(nbd)Cl] ₂	DMI	100	63	964	-	Methanol
16	[Rh(nbd)Cl] ₂	DMI	100	5	369	SiO ₂	Methanol
17	[Rh(cod)Cl] ₂	DMI	53	2	121	SiO ₂	Water
18	[Rh(cod)Cl] ₂	DMI	79	20	464	-	H ₂ O/SDS ^d
19	[Rh(cod)Cl] ₂	DMI	62	10	235	SiO ₂	H ₂ O/SDS ^d
20	[Rh(cod)Cl] ₂	DMI	96	33	508	-	H ₂ O/TX-100 ^d
21	[Rh(cod)Cl] ₂	DMI	63	10	300	SiO ₂	H ₂ O/TX-100 ^d

^a Reaction conditions: 15.4 mmol substrate, 0.022 mmol [Rh(cod)Cl]₂, 0.044 mmol BPPM, 100 mL solvent, 1.1 × 10⁵ Pa H₂, 800 rpm, 30 °C.

^b Rh content was obtained from ICP measurements, the turnover frequency is calculated as follows: $TOF = (n_{Product}/n_{Rh}) \times t$.

^c All results were obtained from GC measurements.

^d 10 g/L surfactant.

^e 1 g/L surfactant.

^f The used microemulsion consists of 77 wt% cyclohexane, 5 wt% water, 9 wt% TX-100 and 9 wt% pentanol [14].

Triton X-100 (TX-100) surfactant (HLB = 13.5) or cationic cetyltrimethyl-ammonium bromide CTAB (HLB = 12) with lower HLB value (hydrophilic lipophilic balance) increases the reaction rate compared to the reaction in water or aqueous solution of hydrophilic SDS surfactant (HLB = 40).

The reaction rates of the hydrogenation of dimethyl itaconate in methanol and in aqueous-micellar solution with TX-100 surfactant are comparable. But the main disadvantage of using of micellar solutions for this reaction with heterogeneous catalyst is the decreased enantioselectivity (Table 3). Only the reactions in micellar solutions with homogeneous catalysts proceed with high enantioselectivities (entries 8 and 10), because the immobilized rhodium complexes are not protected against contact with water by embedding them in the hydrophobic cores of the micelles. This was also shown to be important in a variety of other hydrogenation reactions [13,14,28].

The same phenomenon was reported by Jamis et al. [29,30] for the hydrogenation of α -acetamidocinnamic acid and itaconic acid with catalyst immobilized on sol-gel material or hexagonal mesoporous silica (HMS) in water.

In our process the addition of methanol to an aqueous solution (1:1) (entry 6) or the use of cyclohexane/TX-100/water/1-pentanol microemulsion (entry 12), reported by [23] as alternative reaction media, has increased the reaction rate because more organic solvent was involved in the reaction and increased the solubility of the hydrogen, but it did not improve the enantioselectivity. A successful application of this concept is an EST process (emulsion-solid

transport), which has already been reported in [8] for the Suzuki and Heck coupling reactions with sol–gel immobilized palladium catalysts in microemulsions.

Some results for the hydrogenation of itaconic acid with similar catalysts from the literature are shown in Table 4.

The conversions and enantioselectivities obtained for hydrogenations of itaconic acid and its derivates with sol-gel immobilized Rh/BPPM catalysts in methanol solution are comparable with results in literature obtained with rhodium catalysts immobilized on mesoporous silica. Some of the catalyst could be recycled about 4–8 times without lost in activity and enantioselectivity [32–34]. The hydrogenation reactions in aqueous solutions are not very common. Here the main challenge is still to obtain high enantioselectivity [29,30].

3.7. Catalyst recycling

The replacement of homogeneous catalysts by sol-gel immobilized catalysts allows their reuse and also decreases the costs of the process. In case of an air sensitive in situ formed Rh/BPPM complex the recycling procedure of the catalyst is not very easy. As can be seen in Fig. 8a and b the catalyst could be immobilized in a gel from tetramethyl orthosilicate and tetraethyl orthosilicate as gel building agent, and recycled 3 and 4 times with only small loss in activity and enantioselectivity due to the leaching and catalyst deactivation. About 0.1 mg Rh (4 wt%) and about 0.4 mg P (30 wt%) were

Table 4

Hydrogenation of itaconic acid and derivates with immobilized catalysts (literature).

Substrate	Catalyst	Support	Solvent	X(%)	<i>t</i> (h)	ee (%)	Recycling times	Reference
IA	[Rh(cod)Cl] ₂ /(2S,4S)-BPPM	Ordered mesoporous silica (HMS)	H ₂ O	100	46	23	3	[29,30]
IA	[RhEt ₂ Cl] ₂ /(EtO) ₃ -Si-CH ₂ -PMen ₂	Phosphinated silica (Kieselgel 100)	Methanol	67	20	83		[31]
DMI	$[Rh(cod)_2]^+$ BF ₄ ⁻ /(R,R-MeDuPhos)	Al-MCM-41	Methanol	99	1	99	8	[32]
DMI	RhDuphos/RhBPE	Al-MCM-41/Al-MCM-48/Al-SBA-15	Methanol	100	24	82-99	4	[34]
DMI	[Rh(nbd)Cl] ₂ /(R,R)-BDPBzPSO ₃	MCM-41	Methanol	100	24	53		[20]
DEI (diethyl itaconate)	[Rh(cod)Cl] ₂ -pincer complex	MCM-41	Ethanol	96	2	99	4	[33]



Fig. 8. Recycling of the catalyst after the hydrogenation of itaconic acid in methanol: (a) Rh/BPPM on TMOS-derived silica and (b) Rh/BPPM on TEOS-derived silica. *Reaction conditions*: 15.4 mmol substrate, 0.022 mmol [Rh(cod)Cl]₂, 0.044 mmol BPPM, 100 mL solvent, 1.1×10^5 Pa H₂, 800 rpm, 30 °C.

leached into the solution after the reaction. One part of the catalyst is converted to small black inactive particles, which decrease the activity, reaction rate and enantioselectivity. All recycling experiments were done under N₂ atmosphere to avoid the deactivation of the catalyst by the oxygen from air.

4. Conclusion

The enantioselective hydrogenation of itaconic acid and derivates can be realized in organic solvents like methanol or in aqueous-micellar solutions of different surfactants. The reaction in micellar solutions is more environmentally friendly but tends toward lower enantioselectivities due to the poor interaction between the catalyst and the substrate. Also the choice of different support materials influences the performance of the catalysts. This phenomenon could be explained by hydrophobic and hydrophilic interactions between the substrate and the hydrophobic modified surface of the catalyst. The immobilized catalyst could be recycled several times with only minor decrease in activity and selectivity caused by deactivation and formation of black inactive Rh(0) particles.

Acknowledgment

We gratefully acknowledge the financial support of this study by Deutsche Forschungsgemeinschaft (DFG) through grant SCH0687/8–1.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.10.016.

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