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Investigation of sol-gel supported palladium catalysts for Heck coupling reactions in o/w-microemulsions



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ABSTRACT

Sol-gel supported palladium catalysts are investigated for the Heck coupling reaction between styrene and iodo-/bromobenzene to *trans*-stilbenes in o/w-microemulsions as alternative reaction medium. High conversions and selectivities are obtained with these catalysts and they show better catalytic performance than their commercial analogs Pd@SiO₂ or Pd/C. The influence of the catalyst structure on the activity is investigated in detail showing mass transport limitations that can be optimized by the palladium loading. The catalyst is recyclable >6 times with negligible palladium leaching into the solution. Because of the good recyclability under retention of activity and selectivity, the influence of transport limitations is suppressed and the total catalyst efficiency is increased to more than 2.

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1. Introduction

A general trend in catalysis is the immobilization of homogenous catalyst complexes or metal nanoparticles on solid supports in order to obtain high turnover numbers by facilitating the catalyst recycling. The recycling becomes more important with increasing catalyst costs and decreasing catalytic activity. Especially in important organic transformations, e.g. coupling reactions, an active and stable supported catalyst would allow for continuous reaction processes and definitively lead to higher added values. An often investigated coupling reaction is the Heck reaction and as supported catalysts highly active zeolite PdCl₂-CsX [1] or Pd-NaY [2], magnetically recyclable palladium nanoparticles [3–5], palladium immobilized on carbon [6] or on different modified silica's [7–9] have been investigated. The main criteria for the selection of support materials are the activity of the prepared catalysts and the extent of leaching of the active component into the reaction solution. For example, palladium catalysts immobilized on zeolite are more active than on silica, but they show higher leaching [10]; therefore, silica is often used as support material. Rhodium and palladium catalysts immobilized on silica via the sol-gel method can be used in a variety of catalytic reactions including hydrogenation [11], hydroformylation [12,13], disproportionation [14], isomerization [15], aldehyde decarbonylation [16] and coupling reactions [17], and almost all cases the catalyst retained its activity in consecutive runs.

Not only the structure and morphology of the heterogeneous catalyst is responsible for its activity but also the choice of the solvent. Commonly organic solvents are applied as typical reaction medium, but in the recent years the use of aqueous solutions as solvents has increased [6,18–20] due to the more environmentally friendly properties of water. Unfortunately, reactions with hydrophobic reactants, as used in Heck reactions, cannot be performed in water due to the low solubility of the reactants. For this reason the addition of solubilizers is recommended. Typical solubilizers are surfactants. At concentrations above the critical micelle concentration (*cmc*), the surfactants form micelles, large supramolecular aggregates which consist of hydrophilic head groups directed to water and hydrophobic cores able to solubilize the hydrophobic reactants and the resulting products.

In this contribution we perform Heck reactions in a surfactant system with sol-gel supported catalysts. The mechanism of a heterogeneously catalyzed reaction in micellar systems is complicated due to the inhomogeneous distribution of the reactants within the micro-heterogeneous reaction medium. Therefore many factors influence the course of the reaction. From Scheme 1 it can

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Scheme 1. Mechanism of the sol-gel supported catalysis in microemulsion as reaction medium.

be primarily expected that the structure of the sol-gel immobilized catalyst influences the reaction rate. The structure depends on the nature of entrapped metal nanoparticles, the gel-building agent and on the modification of the support surface. Additionally, the choice of the solvent (surfactant, cosurfactant) and substrate type is crucial for optimizing the reaction conditions.

In this contribution we apply sol–gel supported palladium catalysts and study the influence of the support materials, catalyst precursors, surfactants, solvents and substrates on the activity and selectivity of the Heck reaction of halobenzene and styrene (Scheme 2). The more thermodynamically stable *E*-(*trans*)-stilbene product is favored (>99%) which can be applied further for the synthesis of fine chemicals, e.g. resveratrol [21,22]. Furthermore, for a detailed comparison, unsupported palladium catalysts are investigated for the same reaction. Finally, the heterogeneity of the supported catalysts, the influence of the pore structure and their recycling behavior are studied.

2. Experimental

2.1. Chemicals

2-Bromobenzonitrile, 2-chlorotoluene, methylcinnamate, *trans*- α -methylstilbene, palladium on silica powder (Pd@SiO₂, 5 wt% Pd) and palladium(II) bromide (PdBr₂) were purchased from abcr GmbH & Co. KG Karlsruhe/ Germany. 1-(Tetradecyl)trimethylammonium bromide (TTAB) was obtained from Alfa Aesar Company Karlsruhe/Germany. Sodium dodecylsulfate (SDS) was obtained from AppliChem GmbH Darmstadt/Germany. 30 mol-% 3,3',3"-phosphinidynetris (benzenesulfonic acid) trisodium salt solution (TPPTS) was obtained from Celanese Corporation Irving/USA. Cinnamic acid (CA), 2-ethylhexylacrylate and styrene were purchased from Fluka. Acrylic acid (AA), polyoxyethylen (23) laurylether (Brij[®]35) and palladium on activated carbon (Pd@C, 10wt% Pd) were ordered from Merck KGaA Darmstadt/Germany. Acetonitril (ACN), dimethyl formamide (DMF) and water (HPLC grade) were purchased from Carl Roth GmbH & Co. KG Karlsruhe/Germany. Marlipal 24/60 was provided from Sasol Germany GmbH Marl/Germany. α -Methylstyrene, 4-bromoacetophenone, bromobenzene (PhBr), 4-bromobenzylamine, 1-bromo-4-iodobenzene (IPhBr), tertbutylmethacrylate, 4-chloroacetophenone, chlorobenzene (PhCl), 2-chloro-benzonitrile, 2-chloro-1,3-dimethylbenzene, 1-chloro-2nitrobenzene, 4-chlorostyrene, trans-4-chlorostilbene, dodecyltrimethylammonium bromide (DTAB), hexadecyltrimethylammonium bromide (CTAB), 2-hydroxyethylmethacrylate, IGEPAL CA-520, iodobenzene (PhI), palladium (1000 mg/L) and phosphor (1000 mg/L) ICP standard solutions, methacrylic acid, methylacrylate, α -methylcinnamic acid, methylmethacrylate, methyl- α -methyl-cinnamate, palladium on alumina powder (Pd@Al₂O₃, 1 wt%), palladium(II) acetate (Pd(OAc)₂), poly(4vinylpyridine) (PvyPy), potassium carbonate (K₂CO₃), tetramethyl orthosilicate (TMOS), *trans*-stilbene, triethoxyphenylsilane (PhSi(OEt)₃), trimethoxy(octyl)-silane (OcSi(OMe)₃), dioctyl sodium sulfosuccinate (DSS), Triton X-100 (TX-100) and 4,5bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) were obtained from *Sigma*-Aldrich Company Munich/Germany. *Trans*-4-bromostilbene and *trans*-4-chlorostilbene were purchased from *TCI Europe* Eschborn/Germany.

2.2. Synthesis of sol-gel supported palladium catalysts

The synthesis is comparable to the procedure reported by Rozin-Ben Baruch et al. [17]. Entrapment of the catalyst within hydrophobic silica sol-gel matrix was carried out as follows: trimethoxy(octyl)silane (2.1 mL, 9.877 mmol) or triethoxyphenylsilane (1.612 mL, 6.680 mmol) was hydrolized in 0.4 mL distilled water and 4.25 mL methanol or ethanol for 24 h. Then separately a solution of tetramethyl orthosilicate (3.6 mL 22.961 mmol) was stirred in 2.4 mL methanol and 2 mL water for 20 min. Both solutions were combined and stirred for another 30 minutes to produce the hydrophobically modified silane. Palladium(II) acetate (30 mg, 0.134 mmol) or palladium(II) bromide (35 mg, 0.134 mmol) was dissolved in 4 mL dichloromethane and stirred for 20 minutes. After this step, the catalyst solution was combined with the solution of the hydrophobically modified silane and the mixture was shaken until gelation. Thereafter, the gel was first dried for 4-6 h at $80 \degree C$ and then it was dried for another 8-10h at $80 \degree C$ and 10³ Pa to remove the solvents. The catalyst was washed carefully with boiling dichloromethane and dried again at 80 °C and 10³ Pa for 8-10 h. After the immobilization procedure about 2.2-2.4 g of black-colored sol-gel supported palladium catalyst was obtained.

Palladium catalyst immobilized on hydrophilic support was prepared without addition of trimethoxy(octyl)silane or triethoxyphenylsilane to the hydrolyzed tetramethyl orthosilicate solution.

For the immobilization of palladium catalysts in the presence of phosphine ligands (1:1 ratio) the following modification was done: palladium acetate (11.8 mg, 0.052 mmol) and Xantphos (30.420 mg, 0.052 mmol) or TPPTS (0.508 g, 0.052 mmol) were mixed with 4 mL dichloromethane and stirred for 6 h.

2.3. Reaction procedure

A typical Heck reaction was performed in a double walled glass reactor with reflux condenser at ambient pressure. $153 \,\mu L$



Scheme 2. Heck reaction.

(1.34 mmol) alkene (e.g. styrene) and 158 μ L (1.50 mmol) aryl halide (e.g. iodobenzene) were dissolved in 46 mL organic solvent or aqueous microemulsion in the presence of 0.276 g (2.00 mmol)K₂CO₃ as base and stirred at desired reaction temperature.1.2–1.4 g of the immobilized catalyst containing 15 mg (0.067 mmol) Pd(OAc)₂ on silica was added to the reaction mixture and the reaction was started. For the Heck reaction with homogeneous catalyst only 15 mg (0.067 mmol) of palladium (II) acetate was added. The reaction progress was monitored by measuring the reactant concentrations at different reaction times by high performance liquid chromatography (HPLC).

The used one phase microemulsion consists of CTAB (1.510 g, 3.3 wt%) as surfactant, 1-propanol (3.020 g, 6.6 wt%) as cosurfactant, H_2O (40.855 g, 89.3 wt%) and organic substrates e.g. iodobenzene and styrene (2.84 mmol, 0.8 wt%).

The composition of the microemulsion is usually described by the parameters α (oil ratio), γ (surfactant ratio) and δ (cosurfactant ratio). For the used microemulsions α , γ and δ were 0.9 wt%, 9.9 wt% and 66.7 wt%, respectively.

For the calculation of the parameters, Eqs. (1)-(3) were used.

$$\alpha = \frac{m_{oil}}{m_{oil} + m_{H_2O}} \tag{1}$$

$$\gamma = \frac{m_{surfactant} + m_{cosurfactant}}{m_{surfactant} + m_{cosurfactant} + m_{H_20} + m_{oil}}$$
(2)

$$\delta = \frac{m_{cosurfactant}}{m_{surfactant} + m_{cosurfactant}}$$
(3)

The conversions of reactants and yields of the products were calculated from the concentrations determined by HPLC analysis using the following equations:

$$conversion X(t) = \frac{c_{o,styrene} - c_{t,styrene}}{c_{o,styrene}} \cdot 100$$
(4)

yield
$$Y(t) = \frac{c_{t,stilbene}/M_{stilbene}}{c_{o,styrene}/M_{styrene}} \cdot 100$$
 (5)

The amount of catalyst and ligand that leached from the immobilized catalyst into the reaction mixture after the coupling reaction was measured by ICP. The formed *trans*-stilbene was separated from the microemulsion by extraction with heptane or dichloromethane, followed by solvent evaporation.

2.4. Instruments

The dissolution of palladium from the 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 mixed with 12 mL of a HNO₃/HCl/H₂SO₄ solution (2eq/6eq/4eq). After the microwave treatment, the solid white silica was removed by filtration and the residual solution was analyzed for palladium or/and phosphorus contents using a Varian 715-ES Optical Emission Spectrometer (ICP-OES). Calibration of

the instrument was performed with commercial palladium and phosphorus standards.

The compositions of samples withdrawn from the reaction mixture were determined by HPLC using an Agilent instrument with 250×4 mm chromatographic column Multospher 120 RP18-5 μ from Ziemer Chromatographie Langerwehe/Germany. A mixture of acetonitrile/water (70 vol%/30 vol%) was used as eluent, the flowrate was 1 mL/min, wavelengths were λ = 225 nm and 275 nm, $t_{measurement}$ = 11 min, T = 25 °C and injection volume was 10 μ L.

Specific surface area and pore size distribution of sol-gel immobilized and commercial palladium catalysts were obtained by N₂ adsorption measurements (N₂-BET) using a Micromeritics Gemini 1325 instrument. Transmission electron microscopy was performed with a conventional LaB₆-TEM Tecnai G²20 S-TWIN instrument (FEI Company, USA) operated at 200 kV and equipped with EDAX-EDS for identification of elemental compositions.

High resolution XPS measurements were performed with a Kratos Axis ultra X-ray photoelectron spectrometer for the determination of the oxidation state of palladium. The spectra were acquired with monochromatic AlK α (1486.7 eV) X-ray source with 0° take off angle. The pressure in the test chamber was maintained at 1.99 × 10⁻⁷ Pa during the acquisition process. Data analysis was performed with Vision processing data reduction software (Kratos Analytica Ltd. and Casa SPX Software Ltd.).

The size of palladium particles and the structure of the palladium acetate immobilized on PhSiO₂ were determined by X-ray diffraction measurements (XRD) in X-ray apparatus (D8 Bruker Advance) with KFL Cu 2k X-ray tube as source and Lyux Eye Detector. The samples were previously dried and pulverized.

Effective diffusion coefficients D_{eff} were determined by a method used for porous materials in the construction chemistry [23]. For this purpose the immobilized catalysts were stored in an aqueous SrCl₂ solution for 24 h under N₂. Then they were filtered and placed in a stirred glass reactor with pure water. The increase in electrical conductivity $\kappa(t)$ due to the diffusion of the salt ions out of the pores into the solution was measured at 25 °C. The measured diffusion coefficient D (Eq. (6)) was calculated from the slope m (Eq. (7)) of the semilogarithmic plot (see Fig. S2b in Supporting Information) of the relative conductivity change against time, where r is radius of the catalyst nanoparticles:

$$D = \frac{m \cdot r^2}{\pi^2} \tag{6}$$

$$m = \frac{d \ln((\kappa(t) - \kappa_{end})/(\kappa_0 - \kappa_{end}))}{dt}$$
(7)

3. Results

3.1. Catalyst characterization

The mechanism of the sol-gel process was considerably described in the literature by Avnir [24], Landau [25] and Schmidt [26]. In our case palladium precursor was entrapped into a hydrophobically modified silane matrix, which was formed from a mixture of the hydrolized hydrophilic tetramethyl orthosilicate and



Scheme 3. Entrapment of catalyst into sol-gel matrix with R¹ = Ph or Oc and R = Et or Me.

hydrophobic triethoxyphenyl- or trimethoxyoctyl-silane according to the steps shown in Scheme 3.

During the catalyst entrapment, red palladium (II) species turned in black palladium (0) nanoparticles. Measurements were done to analyze the oxidation state of the immobilized palladium catalyst. Binding energy peaks at 335 eV and 340.471 eV were detected, which are characteristic for $3d_{5/2}$ and $3d_{3/2}$ Pd(0) species. The resulting palladium acetate loading on support material was 0.8-1.1 wt% and was determined from microwave decomposition of the catalyst followed by ICP measurements. No leaching of the palladium was detected after the washing steps with dichloromethane. From these results the immobilization efficiency $\eta_{\text{immobilization}}$ of the catalyst can be estimated to be 1. Specific surface areas of all catalysts are shown in Table 1. For the hydrophobic surface modification essentially phenyl groups were chosen to provide a good compatibility with the aromatic reactants. Octyl modified and unmodified catalysts were prepared for comparison studies. From Table 1 it can be seen that BET surface areas of sol-gel

Table 1

Specific surface areas A of supported palladium catalysts.

Catalyst	Support	<i>A</i> [m ² /g]
$Pd(OAc)_2$	PhSiO ₂	225.0
	PhSiO ₂	249.7
Pd(OAc) ₂ ^a	PhSiO ₂	110.2
Pd(OAc) ₂ ^b	PhSiO ₂	66.7
Pd(OAc) ₂	OcSiO ₂	22.8
	OcSiO ₂	4.2
Pd(OAc) ₂	SiO ₂	338.2
	SiO ₂	386.5
PdBr ₂	PhSiO ₂	216.3
Pd ^c	SiO ₂	254.7
Pd ^c	С	792.6
Pd ^c	Al_2O_3	160.9

^a TPPTS as ligand.

^b Xantphos as ligand.

^c Commercial catalyst.

immobilized catalysts are in the range 200–300 m²/g. The average pore size of the immobilized palladium catalyst was \leq 2 nm and pore volume $V_{\text{pore}} \approx 0.176 \text{ g/cm}^3$. Only for OcSiO₂, Pd(OAc)₂@ OcSiO₂ and in the presence of phosphine ligands, the surface areas were significantly decreased. These results can be explained due to the differences in the formed structures of sol–gel materials containing octyl moieties [27].

Transmission electron microscopy image of the immobilized $Pd(OAc)_2$ catalyst is shown in Fig. 1. The catalyst has many small pores with an average pore diameter of 1–5 nm as it was already seen from the BET measurements. The entrapped palladium nanoparticles with the metallic fcc structure were identified



Fig. 1. TEM image of palladium (II) acetate@PhSiO₂.



Fig. 2. Comparison of (a) catalyst/ligand precursors immobilized on hydrophobically modified PhSiO₂ surface in coupling of bromobenzene with styrene and (b) catalyst/substrate interactions (1.34 mmol alkene, 1.5 mmol PhX, 0.276 g K₂CO₃, 15 mg PdX₂@PhSiO₂, 46 mL microemulsion, 80 °C, AA = acrylic acid).

from the XRD patterns (see Fig. S1 in Supporting Information). From line shape analysis an average diameter for the Pd particles of 3.0 ± 0.3 nm was derived with the Scherrer equation.

3.2. Catalytic activity of the sol–gel immobilized palladium composites

To optimize the reaction conditions, Heck coupling of bromobenzene and styrene to *trans*-stilbene was performed with heterogeneous sol–gel immobilized palladium catalysts prepared from different orthosilicate precursors (Fig. 2a). In comparison to Pd(OAc)₂, the reaction rate with PdBr₂ as precursor was slower by a factor of about 2. No improvement of the catalytic performance was obtained when the palladium catalysts were modified with water soluble ligand TPPTS or with Xantphos. The decrease in activity by using a metal-ligand complex can be explained by hindered access of reactants or retarded catalyst dynamics due to the large structure inside the pores of the catalyst. The ligand modified catalysts were also not very stable and ligand leaching into the solutions occurred.

Catalysts prepared from PdBr₂ or Pd(OAc₂) as precursor were also tested for the coupling of more reactive iodobenzene with styrene or acrylic acid (Fig. 2b). In contrast to bromobenzene, similar conversions were obtained in the coupling reaction with iodobenzene regardless the used precursor. The lower reaction rate for the coupling of bromobenzene with styrene catalyzed by



Fig. 3. Comparison of commercial and sol-gel immobilized catalysts (a) bro-mobenzene/styrene and (b) iodobenzene/styrene (1.34 mmol alkene, 1.5 mmol PhX, 0.276 g K₂CO₃, 15 mg PdX₂@support, 46 mL microemulsion, 80 °C).

 $PdBr_2@PhSiO_2$ can be explained by a lower reactivity of the bromobenzene.

The commercial catalysts tested in this reaction were very stable and no metal leaching was detected. However, the coupling of bromobenzene and styrene with these catalysts was very slow in comparison to the sol–gel immobilized catalysts (Fig. 3a). These commercial catalysts are commonly applied for the hydrogenations of unsaturated substrates and are not suitable for the coupling reactions.

The same catalysts were tested for the coupling of more reactive iodobenzene and styrene. The results are shown in Fig. 3b. Here, we found that the reaction rates with commercial catalysts were much higher than in the Heck coupling of bromobenzene and styrene. The reaction rate with Pd@Al₂O₃ as catalyst was comparable to the sol-gel immobilized catalyst. Therefore, the commercial catalysts can be applied for Heck reaction. However, the reaction rate mainly depends on the type of substrate. Furthermore, their reactivity is lower compared to the hydrophobically modified sol-gel catalysts. The strong difference in the behavior of the commercial catalysts with certain substrates is unexpected and very difficult to predict.

3.3. Effect of the surfactant

As it was shown in Scheme 1, beside the parameters determined by the preparation of the sol-gel immobilized Pd catalyst also the selected solvent is important for the total catalytic performance. In

Table 2

Structures and characteristic properties of the surfactants.

Surfactant	Structure	Туре	<i>cmc</i> [gL ⁻¹] [43,44]	<i>d</i> _{micelle} [nm] [43,44]
SDS		Anionic	2.250	2.06
СТАВ		Cationic	0.330	5.39 (4.3) [45]
Triton TX-100	Man → O → O → O → H	Nonionic	0.325	8.68
TTAB		Cationic	1.344	3.84 [45]
Igepal CA-520		Nonionic		
DSS		Anionic	1.267 [46]	
DTAB		Cationic	4.330	3.34 [45]
Marlipal 24/60	hO→6OH n=6-7	Nonionic	0.012	
Brij®35	0-1-123-OH	Nonionic	0.016	7.94

Section 3.2 we studied the influence of the Pd precursor and silica support, and we could find optimized conditions with respect to the catalyst synthesis. For the solubilization of the hydrophobic reactants in an aqueous environment, surfactants can be used. The interactions between the silica support and formed micellar aggregates will also affect the reaction rate. Therefore, Heck reaction was investigated in aqueous microemulsions with different anionic, nonionic and cationic surfactants. Their structures, critical micelle concentrations (*cmc*) and the average diameter of the micelles ($d_{micelle}$) measured in aqueous-micellar solutions are given in the Table 2.

All microemulsions were transparent and homogeneous except microemulsions containing DSS or Igepal CA-520 as surfactant. As can be seen from Fig. 4, a broad variety of surfactants can be applied for the formulation of the reaction medium. Full conversion was obtained after 6–7 h with cationic CTAB, nonionic Triton TX-100 and anionic SDS as surfactants. The conversion increases with increasing C-chain length, decreasing HLB-value (hydrophilic–lipophilic balance) and decreasing *cmc*, if homologue series of cationic surfactants CTAB, TTAB and DTAB were used: $C_{16} >> C_{14} \approx C_{12}$. The most hydrophobic surfactant CTAB is preferred because of the more hydrophobic micelle cores ($d_{micelle}$) and largest



Fig. 4. Influence of HLB values of surfactants on the conversion of the Heck reaction $(1.34 \text{ mmol styrene}, 1.5 \text{ mmol bromobenzene}, 0.276 g K_2 CO_3, 15 mg Pd(OAc)_2@PhSiO_2, 46 mL microemulsion, 80 °C).$

Table 3 Substrate variation



Entry	Х	Y	W	Product	Reaction time t (min)	Yield Y (%)
1	Cl	Н	-COOH	Cinnamic acid	429	70
2	Br	Н	-COOH	Cinnamic acid	396	76
3	Ι	Н	-COOH	Cinnamic acid	359	98
4	Ι	Br	-COOH	4-Bromocinnamic acid	513	77
5	Br	Н	-COOMe	Trans-methylcinnamate	372	45
6	Ι	Н	-COOMe	Trans-methylcinnamate	407	72
7	Br	Н	-COOCH2-CH(Et)(Bu)	2-Ethylhexylcinnamate	359	64
8	Ι	Н	-COOCH2-CH(Et)(Bu)	2-Ethylhexylcinnamate	451	82
9	Br	Н	α-Me-COOH	α-Methylcinnamic acid	389	64
10	Ι	Н	α-Me-COOH	α-Methylcinnamic acid	477	62
11	Br	Н	α-Me-COOMe	Methyl-(E)- α -methylcinnamate	339	46 ^b
12	Ι	Н	α-Me-COOMe	Methyl-(E)-a-methylcinnamate	435	54 ^b
13	Br	Н	α-Me-COO ^t Bu	(E)- ^t Butyl-2-methyl-3-phenylacrylate	387	45
14	I	Н	α-Me-COO ^t Bu	(E)- ^t Butyl-2-methyl-3-phenylacrylate	422	89
15	Br	Н	α -Me-COO(CH ₂) ₂ -OH	2-Hydroxyethyl-(E)-α-methylcinnamate	407	50
16	I	Н	α -Me-COO(CH ₂) ₂ -OH	2-Hydroxyethyl-(E)-α-methylcinnamate	485	70
17	Cl	Н	Ph-	Trans-stilbene	327	62
18	Br	Н	Ph-	Trans-stilbene	555	100
19	Ι	Н	Ph-	Trans-stilbene	480	94
20	I	Br	Ph-	4-Trans-bromostilbene	398	89
21	Br	Ortho-NH2-CH2-Ph-	Ph-	4-[(1E)-2-(phenyl)ethenyl]-benzenemethanamine	458	57
22	Cl	Ortho-CN-Ph-	Ph-	2-Trans-cyanostilbene	433	41
23	Br	Ortho-CN-Ph-	Ph-	2-Trans-cyanostilbene	393	59
24	Cl	Ortho-Me-Ph-	Ph-	Trans-2-methylstilbene	477	44
25	Cl	Ortho-Me-Ph-	Ph-	2,6-Trans-dimethylstilbene	367	55
26	Cl	MeOCPh-	Ph-	4-Trans-acetylstilbene	444	65
27	Br	MeOCPh-	Ph-	4-Trans-acetylstilbene	446	60
28	Cl	Styrene	Ph-	Distyrylbenzene	419	0
29	Br	Styrene	Ph-	Distyrylbenzene	448	20
30	Br	Н	Para-Cl-Ph-	4-Trans-chlorostilbene	371	50
31	Ι	Н	Para-Cl-Ph-	4-Trans-chlorostilbene	415	92
32	Br	Н	α-Me-Ph-	α-Methylstilbene	377	32 ^b
33	Ι	Н	α-Me-Ph-	α-Methylstilbene	318	65 ^b

^a *Reaction conditions*: 1.5 mmol olefine, 1.34 mmol alkene or styrene, 2 mmol K₂CO₃, 1.25 wt% Pd(OAc)₂@ PhSiO₂ (0.067 mmol Pd(OAc)₂), 46 mL microemulsion (3.3 wt% CTAB, 89.3 wt% H₂O, 6.6 wt% propanol), 80 °C.

^b 1:1 product: terminal olefine

storage capacity for the substrates. Predictions cannot be done for the behavior of the other not homologue surfactants in this reaction because of their different structures. There is also no dependence on the type of the surfactant and the reaction rate.

3.4. Substrates

To extend the scope of the protocol, we applied the palladium(II) acetate immobilized on hydrophobically modified silica catalyst to screen for a wide variety of substrates. A screening of aryl halides Y-Ph-X shows that this catalytic system is suitable for all kinds of aryl halide. It results in the expected ranking with higher reactivity of iodobenzene than bromobenzene, 1-bromo-4-iodobenzene (with 4-bromo-*trans*-stilbene as product) and lowest reactivity of less active chlorobenzene as can be seen from Table 3. These results are typical for the reaction of aryl halide with styrene (Entry 17–20), acrylic acid (Entry 1–4) and methacrylic acid (Entry 9–10).

Because of the mechanistic aspects of Heck coupling, *trans*products are favored. The reactivity of styrene is higher than that of 4-chlorostyrene and α -methylstyrene (with terminal olefins as by products 1:1) as shown in Table 3 (Entry 30–33) for the reaction with iodo- and bromobenzene. Also different aromatic ortho- and para- substituted aryl halides Y-Ph-X react with styrene to *trans*-stilbene derivates. The reactivity decreases if the para-substituted substrates (e.g. para-iodobromobenzene) are applied in the reaction (Table 3 Entry 21–29) and is very small with the ortho-substituted substrates (e.g. ortho-methylchlorobenzene). The reaction rate depends not only on the position of the substituent, but also on the substituent type. Substituents with electron withdrawing groups (e.g. cyano or acetyl group) are more active than these with electron donating groups (e.g. methoxy or methyl group).

The nonaromatic acrylic acid shows good reactivity with iodobenzene and its reactivity is comparable to aromatic styrene. The more sterically hindered methacrylic acid and derivates were less reactive (Table 3 entry 5–16) and side-products were formed. The arylation of medically interesting 1,1-substituated olefine like methacrylate or α -methylstyrene can afford different products in dependency of the direction of the β -H-elimination: the main desired product α -methylcinnamate with *E*- or *Z*-stereochemistry or a by-product α -benzylacrylate with a terminal double bond. The product and by-product ratio was 1:1.

All substrates tested in Heck coupling reaction in aqueous microemulsions show similar reactivities as in commonly used organic solvents, e.g. dimethylformamide or acetonitrile, at higher temperatures. For the following investigations only the reactions of styrene and iodo- or bromobenzene to *trans*-stilbene were considered.



Fig. 5. Influence of the hydrophobicity of the sol-gel support on the catalytic activity $(1.34 \text{ mmol styrene}, 1.5 \text{ mmol bromobenzene}, 0.276 g K_2CO_3, 15 \text{ mg} Pd(OAc)_2@$ support, 46 mL microemulsion, 80 °C).

3.5. Effect of surface modification

As shown in Section 3.2, Figs. 2 and 3, various commercial and synthesized palladium catalysts were tested for the Heck coupling. $Pd(OAc)_2$ immobilized on $PhSiO_2$ was the choice of catalyst for further investigations, because of its high stability and reactivity. The influence of different silica support materials on the reaction rate was also studied. In addition to the nonmodified sol-gel prepared from tetramethyl orthosilicate alone, two hydrophobically modified sol-gel matrices were prepared using octyl and phenyl substituted alkoxysilane precursor.

The adsorption of the aromatic compounds used in the reaction was stronger if catalysts immobilized on hydrophobic support were used. The inverse adsorption effect was already shown in our previous publication about the enantioselective hydrogenation of itaconic acid and derivates [28]. The hydrogenation of hydrophilic nonaromatic substrates is favored using Rh/BPPM catalysts immobilized on hydrophilically modified sol-gel materials. Whereas the reaction is much slower when performed using hydrophobically modified surfaces. The transport processes of the reactants in the catalyst pores can be described by the diffusion coefficients D_{eff,tracer} which were calculated from diffusion measurements with SrCl₂ salts as tracers [29]. From the diffusion coefficients D_{eff,tracer} it is also clear that the adsorption of the substrates on hydrophilic surfaces is smaller than on hydrophobically modified surfaces (see Fig. S2a and b in Supporting Information). The determined diffusion coefficients $D_{\rm eff,tracer}$ show the following ranking: SiO_2 (8.1 × 10⁻⁹ cm² s⁻¹) < OcSiO₂ $(1.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}) \ll \text{PhSiO}_2 (4.7 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}).$

As shown in Fig. 5, the hydrophobicity of the sol-gel affects the reaction rate and conversion of the palladium catalyzed coupling of bromobenzene and styrene. The best results were obtained when phenyl moiety was introduced, followed by octyl modified catalyst. The reaction was the slowest when hydrophilic modification was applied.

To examine the influence of the diffusion of the reactants inside the catalyst pores on the reaction rate, the ratio of the reaction time constant and the diffusion time constant are estimated and expressed as the Weisz modulus Ψ . This is a characteristic parameter to test for mass transfer limitations on heterogeneously catalyzed reactions and can be calculated using the Weisz–Prater criterion [15,30]:

$$\Psi = L_{cat}^2 \cdot \frac{n+1}{2} \cdot \frac{r \cdot \rho_{cat}}{c_o \cdot D_{eff,styrene}}$$
(8)

Table 4

Weisz-modulus for the Pd(OAc)₂ catalysts immobilized on silica.

Material	$D_{\rm eff}$, styrene [cm ² s ⁻¹]	$r_0 [\operatorname{mol} l^{-1} \cdot \mathbf{s}^{-1}]$	Weisz-Modulus Ψ
Pd(OAc) ₂ @SiO ₂ Pd(OAc) ₂ @PhSiO ₂ Pd(OAc) ₂ @OcSiO ₂	$\begin{array}{c} 6.0\times 10^{-10} \\ 1.2\times 10^{-9} \\ 3.6\times 10^{-9} \end{array}$	$\begin{array}{l} 7.5\times 10^{-7} \\ 2.3\times 10^{-6} \\ 3.0\times 10^{-6} \end{array}$	4 3 5

In Eq. (8), L_{cat} is radius of the catalyst nanoparticles, n is reaction order, r is the reaction rate, ρ_{cat} is density of the catalyst, c_0 is initial styrene concentration and $D_{eff,styrene}$ is effective diffusion coefficient of styrene. For $\Psi \ll 1$ no diffusion limitation influences the reaction. For our discussion the measured diffusion coefficients $D_{eff,tracer}$ of SrCl₂ were transferred in the effective diffusion coefficients of styrene $D_{eff,styrene}$ according to the ratio of the molecular diffusion coefficients at ambient temperature in water ($D_{M,tracer} = \text{SrCl}_2 = 1.4 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ [31] and $D_{M,styrene} = \text{styrene} = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [32]):

$$D_{eff,styrene} = D_{M,styrene} \cdot \frac{\varepsilon}{\tau} \tag{9}$$

$$\frac{\varepsilon}{\tau} = \frac{D_{eff,tracer}}{D_{M,tracer}} \tag{10}$$

In Eq. (10), ε is the porosity of the immobilized catalyst and τ is the tortuosity.

The porosity of Pd(OAc)₂@PhSiO₂ can be calculated from the ratio of pore volume V_{pore} (BET measurement) to the volume of catalyst resulting in ε = 33.4%. The tortuosity τ describes the way of the diffusion in the pores of the catalyst and can be determined from Equation 10 (τ = 4.689). The pore diameter is 1–2 nm.

The initial reaction rates using different catalysts were determined according to:

$$r_0 = c_0 \cdot \frac{dX}{dt} \tag{11}$$

The average particle size of 200 μ m and ρ_{cat} of 1.9 g/cm³ were considered for all calculations (Table 4).

In our case the Weisz modulus was $\Psi \approx 3$ for the heterogeneous reaction with mostly applied Pd(OAc)₂@PhSiO₂, indicating a substantial limitation of the reaction rate by the diffusion of the reactants inside the pores of the catalyst. This result is also supported by the comparison of the temperature dependency of the heterogeneous and the homogeneous catalysts as will be discussed in Section 3.6. The pore efficiency η_{pore} can be calculated from the Weisz-Prater criterion Ψ for various reaction orders [33]: $\eta_{\text{pore}} = 1$ (for $\Psi < 1$, no diffusion limitations) and $\eta_{\text{pore}} = \Psi^{-1}$ (for $\Psi \ge 1$, diffusion limited reaction). From the correlation for $\Psi \ge 1$, for the applied Pd(OAc)₂@PhSiO₂ catalysts a value of about 40% is obtained for η_{pore} . By decreasing the Pd(OAc)₂ loading on silica material from 1.2% to 0.5%, the specific productivity of the palladium was increased by a factor of 2 from 2.5 × 10⁻⁴ to 5 × 10⁻⁴ mol/g_{Pd}·min (see Fig.S3 in Supporting Information).

3.6. Kinetics of the reaction

The coupling of styrene with bromobenzene or iodobenzene is known to follow a second order reaction rate [34,35]. In our studies the reaction rate also increases linearly with the concentrations of both reactants. The distinction has to be drawn between homogeneously (in situ formed not supported palladium (0) nanoparticles) and heterogeneously catalyzed Heck reaction (Pd(OAc)₂ immobilized on silica by a sol-gel method). In comparison to the homogeneously catalyzed reaction, the reaction with sol-gel immobilized catalyst (1.2% Pd(OAc)₂ on phenyl modified silica) is slower at the beginning as can be seen from the measurements at 80 °C shown in Fig. 6a, but finally proceed to reach



Fig. 6. Comparison of homogeneous and heterogeneous catalyzed Heck reactions in microemulsion (a) $X_{styrene}$ -t-curve (80 °C), (b) Arrhenius plot (1.34 mmol styrene, 1.5 mmol PhBr, 0.276 g K₂CO₃, 15 mg Pd(OAc)₂@PhSiO₂ or 15 mg homogeneous Pd(OAc)₂, 46 mL microemulsion).

a higher conversion than the homogeneous catalyst. This experiment was repeated for temperatures ranging from 50 to $90 \degree C$ (for both catalysts).

Activation energies E_A were determined for the coupling of bromobenzene and styrene using homogeneous and heterogeneous catalysts (Fig. 6b) according to Eq. (12):

$$\ln(k) = -\frac{E_A}{R \cdot T} + \ln(k_\infty)$$
(12)

 $E_{A, \text{heterogeneous}} = 60.4 \text{ kJ mol}^{-1}$

 $E_{A, \text{homogeneous}} = 74.5 \text{ kJ mol}^{-1}$

The activation energy of the heterogeneous reaction is lower than that of the homogeneous reaction, because of the diffusion limitation that is much less temperature sensitive than the chemical reaction itself.

It is known that for porous heterogeneous catalysts pore diffusion limitations can lead to lower rates in comparison to the homogenously catalyzed reaction. By adjusting the catalyst size (smaller particles) or temperature (lower temperatures) it is possible to suppress the diffusion limitation effect because the reaction rate is no longer limited to the rate for the transport of reactants. In this case, the catalyst efficiency is comparable to the homogenous catalyst. For supported metal catalysts, in which a metal is the active material, it is possible that the reaction rate remains lower even if diffusion limitation is eliminated because some of the metal can be intercalated and not be available for the reactants. By comparison of the reaction rates for the supported and unsupported



Fig. 7. Recycling of sol-gel immobilized catalyst for (a) iodobenzene, styrene, $Pd(OAc)_2@PhSiO_2$; (b) bromobenzene, styrene, $Pd(OAc)_2@OcSiO_2$; (c) bromobenzene, styrene, $Pd(OAc)_2@PhSiO_2$ (1.34 mmol activated alkenes, 1.5 mmol aryl halides, 0.276 g K₂CO₃, $Pd(OAc)_2@R^1SiO_2$, 46 mL microemulsion, 80 °C).

catalysts, done in the kinetically controlled regime, the impact of intercalation was calculated to be $\eta_{\text{intercalation}} = 0.81$.

3.7. Catalyst recycling

The recycling experiments were carried out for the coupling of bromobenzene or iodobenzene with styrene to produce *trans*-stilbene. Palladium(II)acetate catalysts immobilized on hydrophobic octyl or phenyl modified silica supports could be recycled 6 times without any significant decrease in activity (Fig. 7). Only small amount of palladium leaching into the solution was detected by ICP measurements after each reaction as can be seen in Table 3 and no leaching was detected after second and the following recycling steps.

Table 5	
Catalyst leaching into	the reaction solution.

Catalyst precursor	Support	$g_{Pd(OAc)_2}/g_{support}$ d,e [%]	Leaching after reaction $m_{Pd(OAc)_2 in} \mbox{ solution} / m_{Pd(OAc)_2 \mbox{ catalyst}} \ ^{\rm e} \ \mbox{ [\%]}$
$Pd(OAc)_2$	PhSiO ₂	1.2	0.010-0.012
PdBr ₂	PhSiO ₂	1.2	0.031-0.077
Pd(OAc) ₂ ^a	PhSiO ₂	1.2	0.062 (5.475 ligand)
Pd(OAc) ₂ ^b	PhSiO ₂	1.2	0.068 (7.800 ligand)
Pd(OAc) ₂	OcSiO ₂	1.2	0.013
Pd(OAc) ₂	SiO ₂	1.2	0.013
Pd ^c	SiO ₂	5.0	0
Pd ^c	Charcoal	10.0	0
Pd ^c	Al_2O_3	1.0	0

^a TPPTS.

T-1-1- F

^b Xantphos.

^c Commercial catalyst.

^d Determined by microwave decomposition. ^e Palladium and ligand amount determined from ICP measurements.

Different tests were performed to check if the active catalyst is indeed heterogeneous. First the hot filtration of the catalyst after obtaining a conversion of about 50% was done. Thereafter, the reaction was continued with the residual solution. No further conversion was observed in the reaction as a proof that no homogeneous catalyst was present in the reaction mixture. Also a poisoning test was done with 300 eq of highly cross linked poly(4vinylpyridine) [10,36,37]. This substance can bind to homogeneous Pd(II) species and poisons it, resulting in a decrease in reaction rate. The reaction with heterogeneous catalyst (Pd(OAc)₂@PhSiO₂) showed no decrease in reactivity upon the addition of poly(4vinylpyridine). Also the analysis of the reaction mixtures after the reactions (Table 5) showed only a small amount of leaching of Pd into the solution. From these experiments we conclude that no homogeneous catalyst is involved in the Heck coupling with sol-gel immobilized catalyst in aqueous microemulsion.

From these results the recycling efficiency of the sol–gel immobilized catalyst $\eta_{\text{recycling}}$ can be estimated. For mostly applied Pd(OAc)₂@PhSiO₂ only 0.01% palladium acetate leaching after the first reaction and no further metal leaching was determined afterwards. That's why the recycling efficiency $\eta_{\text{recycling}}$ of the catalyst can be estimated to be 0.999.

4. Discussion

Heck coupling of iodobenzene and styrene catalyzed by sol-gel immobilized palladium (II) acetate represents a good alternative to the commonly used homogeneous, e.g. Pd(dba)₂/phosphoramidite, catalyzed coupling of iodobenzene and styrene in dimethylformamide at 80°C (TOF=315/h) [38]. Also heterogeneously catalyzed reactions, e.g. Heck coupling of styrene and 4bromofluorobenzene catalyzed by palladium immobilized on zeolite at 140 °C in dimethyl acetamide $(TOF_{Pd(0)]-NaY} = 20/h$ and $TOF_{Pd(OAc)2]-NaY} = 2000/h$ [2], or reactions under biphasic conditions, e.g. PdCl₂(bipy) catalyzed coupling of iodobenzene and styrene in n-octane/p-xylene/ethylene glycol at 150°C (TOF = 227/h) [39], were already reported by other research groups. The reactions in conventional solvents at high temperatures, which were already reported in the literature, had higher turnover frequencies. For example, Heck coupling catalyzed by Pd/C in NMP at 150°C [40] had TOF>18,000/h. By lowering the reaction temperature the Turnover Frequency would decrease below $TOF_{80^{\circ}C} = 8-140/h$. On the other hand, a more environmentally friendly process management on the example of Heck coupling in microemulsion with >90% of water at lower temperatures could be shown. In addition to this, the catalyst and product recycling was enabled.

The reaction of iodobenzene and styrene with Pd/C in different aqueous-micellar solutions of cationic surfactants was reported earlier, but no conversions were obtained for the less watersoluble substrates bromo- or chlorobenzene [6]. Heck reaction of iodobenzene and styrene in aqueous-micellar solutions of different surfactants with palladium catalyst and PPh₃ ligand [41] or Suzuki coupling with Pd/C catalyst could also be performed [20]. The addition of small amount of alcohol as a cosurfactant and the formation of aqueous microemulsion is desirable, for example for a Heck reaction in a microemulsion of TX-100/n-heptane/butanol/water/propylene glycol mixture [35]. A comparison of the reaction of styrene and bromobenzene in different reaction media with Pd(OAc)₂@PhSiO₂ is given in Table 6, including some examples from literature.

To clearly show the micellar effect it is common to compare the surfactant system with pure water. Here, the reaction in water was also possible, but the substrates could not be completely solubilized. A small increase in solubility was achieved by adding the hydrophilic surfactant SDS and much higher solubilization was achieved if the hydrophobic surfactant CTAB was added. The full solubility could only be obtained by using an aqueous microemulsion with a short chain alcohol as cosurfactant. Under complete dissolution of the reactants full conversion at 80 °C is obtained in 420 min. We tested the same reaction in different organic solvents instead of microemulsions and activity was much lower. Within the same reaction time, the conversion was only about 30%. As shown by other groups, in organic solvents higher temperatures (about 130–150 °C) are needed to obtain higher conversions.

During the reaction the homogeneous Pd(II) species are reduced to the black active Pd(0) in the presence of surfactant.

The use of the sol-gel immobilized palladium catalyst in the Heck reaction with different substrates is preferable because of the higher activities in comparison to the commercial catalysts. The catalysts can be reused more than 6 times without loss in activity and with only a minor leaching of the palladium species into the reaction solution and can indeed be classified as a heterogeneous catalyst. The separation process (Scheme 4) of the catalyst and product after the reaction is very simple: (a) filtration and reuse of solid catalyst, (b) product separation through extraction with heptane and (c) separation and reuse of surfactant from water, e.g. by micellar enhanced ultra filtration (MEUF) or adsorption on silica or granite sand.

At last the overall efficiency η of porous Pd(OAc)₂ catalyst immobilized on PhSiO₂ was estimated from the different efficiencies, which were calculated above by multiplication of all factors:

 $\eta = \eta_{\text{immobilisation}} \cdot \eta_{\text{intercalation}} \cdot \eta_{\text{pore}} \cdot (> N_{\text{cycle}}) \times \eta_{\text{recycling}}^{(>N)}$ (13)

 $\eta = 1.0.81.0.4.(>6).(>0.999) = (>1.92)$

In Eq. (13), $\eta_{\text{immobilization}}$ and $\eta_{\text{recycling}}$ are palladium acetate leaching fractions into the solution after the catalyst synthesis and after N recycling experiments and were determined from

Table 6

Effect of reaction media on the Heck coupling of bromobenzene and styrene.

Solvent	Catalyst	Base	<i>T</i> [°C]	X [%]	<i>t</i> [min]	Ref.
MeOH ^a	Pd(OAc) ₂ @PhSiO ₂	K ₂ CO ₃	80	10	438	
MeOH ^{a, b}	Pd(OAc) ₂ @PhSiO ₂	K ₂ CO ₃	80	31	380	
DMF ^a	Pd(OAc) ₂ @PhSiO ₂	K_2CO_3	80	30	433	
DMF	PdCl ₂ @zeolite	K_2CO_3	153	74	150	[1]
NMP	Pd@hydroxyapatite	K ₂ CO ₃	130	94	1440	[47]
DMF ^{a,b}	Pd(OAc) ₂ @PhSiO ₂	K ₂ CO ₃	80	17	1335	
DMF ^{a, c}	Pd(OAc) ₂ @PhSiO ₂	K ₂ CO ₃	80	2	1334	
ACN/H ₂ O (1:1) ^a	Pd(OAc) ₂ @PhSiO ₂	K ₂ CO ₃	80	45	420	
H ₂ O ^a	Pd(OAc) ₂ @PhSiO ₂	K ₂ CO ₃	80	88	420	
H ₂ O ^e	Pd@polystyrene	КОН	90	10	1320	[48]
10 g/L CTAB/H ₂ O ^a	Pd(OAc) ₂ @PhSiO ₂	K ₂ CO ₃	80	100	420	
70 g/L SDS/H ₂ O ^a	Pd(OAc) ₂ @PhSiO ₂	K ₂ CO ₃	80	50	360	
CTAB/H ₂ O ^e	Pd@C	K ₂ CO ₃	80	60	240	[6]
CTAB/propanol/H ₂ O ^{a,d}	Pd(OAc) ₂ @PhSiO ₂	K ₂ CO ₃	80	100	420	
TX-100/H ₂ O/[BMIM]PF ₆ ^e	PdCl ₂	NEt ₃	100	100	120	[49]

^a Reaction conditions: 1.5 mmol bromobenzene, 1.34 mmol styrene, 2 mmol K₂CO₃, 1.25 wt% Pd(OAc)₂@PhSiO₂ (0.067 mmol Pd(OAc)₂), V = 46 mL, 80 °C.

^b TPPTS.

^c Xantphos.

 $^d~$ 3.3 wt% CTAB, 89.3 wt% $H_2O,\,6.6\,wt\%$ propanol.

^e Iodobenzene and styrene as reactants.



Scheme 4. Product and catalyst separation.

ICP measurements, N_{cycle} is the number of recycling experiments, $\eta_{intercalation}$ is the efficiency of the immobilized catalysts compared to the homogeneous catalysts and can be estimated from the comparison of reaction rates for homogeneously and heterogeneously catalyzed reaction and η_{pore} is the pore efficiency calculated from the Weisz–Prater criterion Ψ for the second order reaction. For Ψ = 3, the pore efficiency was 40%. Because no deactivation and leaching of the catalyst after sixth recycling step was seen, further application of the catalyst in much more recycling steps can be predicted. That's why the number of the recycling steps was estimated to be >6.

Catalyst efficiencies $\eta \ge 1$ are typical for very stable and active catalysts and demonstrate that palladium acetate immobilized on hydrophobically modified silica by sol–gel method is a good alternative to homogeneous one. In comparison to these results, the catalysts with high metal leaching and low reactivity would show smaller section efficiencies and the complete efficiency of the catalyst would be $\ll 1$.

Of course is the immobilization of homogeneous catalysts disadvantageous in comparison to homogeneous catalysts because of diffusion limitations and decrease in reactivity. But on the other side the possibility to recycle the catalysts more than 6 times increases the efficiency of sol-gel immobilized catalysts enormously and reduces the cost of the complete process.

The Turnover Number (TON) and Turnover frequency (TOF) provides the information about the activity and efficiency of

the catalyst:

$$TOF = \frac{TON}{t} = \frac{n_{\text{product}}/n_{\text{Pd(OAc)}_2}}{t}$$
$$= \frac{(1.34 \text{ mmol})/0.0668 \text{ mmol Pd(OAc)}_2}{6 \text{ h}} = \frac{20.1}{6h} = \frac{3.34}{h} \quad (14)$$

For the most often used $Pd(OAc)_2$ @PhSiO₂, the TON is 20 and TOF is 3.3/h for the reaction of iodobenzene and styrene. For the homogeneous $Pd(OAc)_2$ catalyzed reaction the same results would be obtained. TOF should be >500/h (TON > 1000) for industrially usable catalysts [42]. In Fig. 7 we have shown that $Pd(OAc)_2$ @PhSiO₂ could be recycled more than 6 times without loss in activity. Considering these results the TON would be >501 after 25 runs, which is useful for industrial application. The reactant concentrations can be increased up to 5 times, which would also increase the Turnover Number to TON = 100 after one run up to TON > 1000 for 10 runs.

5. Conclusion

Heck reaction in aqueous microemulsions with $Pd(OAc)_2$ or $PdBr_2$ catalysts immobilized on modified silica support materials is a alternative to the conventional organic solvents. One phase microemulsions (water/propanol/CTAB) with the consistence $\alpha = 0.9\%$, $\gamma = 9.9\%$ and $\delta = 66.7\%$ as reaction media allows a better solubility of hydrophobic substrates in water. To improve

the reactivity of the sol-gel immobilized catalysts the application of hydrophobically modified surfaces (PhSiO₂) is preferred, because of the attractive interactions between the hydrophobic aromatic substrates, e.g. iodobenzene, and the palladium catalyst immobilized on phenyl modified silica. The synthesized catalysts are more active in comparison to commercial catalysts (e.g. Pd@SiO₂ or Pd@C) and can be used in a variety of Heck reactions. These immobilized catalysts could be recycled more than 6 times without loss in activity. No homogeneous species were detected in the reaction mixture, as proved by the heterogeneity tests. Due to the high porosity and the strongly branched pore systems of the sol-gel materials the diffusion of small reactant molecules inside the pore systems was not very high. To obtain a good utilization of the active noble metal immobilized in the support material the loading should be limited to an amount that still guarantees a high effectiveness factor of the composite catalysts (see Fig. S3 in Supporting Information). The influence of the mass transport limitations on the reaction rate can be quantified from the comparison of the activation energies E_A of the coupling reaction between bromobenzene and styrene with sol-gel immobilized catalyst and with homogeneous catalyst. It was also showed that the Weisz-modulus was Ψ > 1. With a well adjusted $Pd(OAc)_2$ loading in the range of 0.5% a highly efficient catalyst was obtained for the reaction tested here that also show stable recycling behavior. The immobilization process of the palladium catalysts was disadvantageous in comparison to homogeneous catalysts. But on the other side the possibility of catalyst recycling more than 6 times compensate this disadvantage and a catalyst efficiency $\eta \gg 1$ could be arrived, which is characteristic for very stable and active heterogeneous catalysts.

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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.2014.06.016.

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