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Dependence of the Heck coupling in aqueous microemulsion by supported palladium acetate on the surfactant and on the hydrophobicity of the support

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ABSTRACT

Heck coupling of aqueous microemulsions of bromobenzene and styrene by palladium acetate entrapped within hydrophobicitized silica sol–gel is associated with the formation of supported Pd(0) nanoparticles that catalyze the process. The efficiency of the coupling strongly depends on the hydrophobicity of the sol–gel matrix. In a series of experiments in which the support was prepared by co-condensation of tetramethoxysilane [$Si(OMe)_4$] and ca. 5% of either alkyl or aryl alkoxysilanes [$R_n(OR')_{4-n}$] the activity of the immobilized catalyst increased along with the increasing length of the hydrophobic alkyl chain R in the alkylalkoxysilane as well as with the increase of n. Hydrophobic aryl groups are superior to alkyl ones but electron-withdrawing substituents on the aryl moieties lower the reactivity. The rate of the coupling process depends also on the nature of the surfactant used to solubilize the reactants. The order of rates is anionic < non-ionic < cationic surfactants. The metallic nanoparticles can be recycled and reused for at least 4–6 further catalytic runs without any loss of catalytic activity.

1. Introduction

Public concern about the large amounts of harmful solvents used in organic synthesis and catalysis led to substantial efforts to replace the traditional media by water. Since many organic reagents are insoluble in aqueous media a variety of methods have been investigated for the solubilization of lipophilic substrates [1]. Our contribution to this field was the development of a unique three phase emulsion/sol–gel system for transport and catalysis (EST). In this system the catalyst is entrapped within the ceramic matrix and the substrates are in the state of an emulsion [2], thus, enabling facile recovery and recycling of the catalyst. Replacement of the emulsion by a microemulsion [3] converts the reaction medium into a highly active system for catalytic hydrogenation of alkenes, arenes, carbonyl- and nitro-compounds, for hydroformylation and for cross-coupling reactions [4–7]. Among the C–C couplings that have been performed in water and gained much interest in the industry are the Heck and Suzuki reactions. (For some critical discussions see Refs. [8–19].) While the mechanistic features of these processes in organic solvents have been studied in depth some of the factors that affect the reactions in *aqueous media* have not yet been investigated and understood [8,20]. We have now investigated the influence of two such factors on the Heck coupling: the effect of the hydrophobicity of the sol–gel matrix in which the catalyst is entrapped, and the nature of the surfactant used to prepare the microemulsions.

2. Experimental

2.1. Instruments

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 instrument in $CDCl_3$. Mass-spectral measurements were performed with a Hewlet-Packard model 4989A equipment with an HP model 5890 series II gas chromatograph. ICP-MS analyses were carried out with a Perkin Elmer model ELAN DRC II instrument. A Micrometrics ASAP 2020 instrument was used for BET-N_2 surface area and pore diameter measurements of the sol–gel matrices. Determination of the micelle size by dynamic scattering experiments was performed with the aid of a 1 W Nd:YAG laser (Compass 150, Coherent, USA) and an ALV 5000/E autocorrelator (ALV, Germany). Gas chromatographic measurements were made with a Hewlet-Packard model Agilent 4890D equipped with a 15 m long capillary column packed with bonded and crosslinked (5% phenyl)methyl polysiloxane [HP-5]. Transmission electron microscopy was done with a scanning transmission electron microscope (STEM) Tecnai G^2 F20 (FEI Com-

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pany, USA) operated at 200 kV and equipped with EDAX-EDS for identification of elemental compositions.

2.2. Chemicals

Bromobenzene, styrene, 1,1-diphenylethylene, L-proline, *E*- and *Z*-stilbene, (tetramethoxy)silane [TMOS], (tetraethoxy)silane [TEOS], (4-chlorophenyltriethoxy)-silane and palladium acetate were purchased from the Sigma–Aldrich company. Propyl-, octadecyl-, 1-naphthyl- and (4-methylphenyltrimethoxy)silane, methyl-, ethyl-, *iso*-butyl (octyltriethoxy)silane [OTEOS] and (phenyltriethoxy)silane, dimethyl- and (diphenyldiethoxy)silane, trimethyl- and (triphenylethoxy)silane were obtained from ABCR (Glest, Inc.). The surfactants were obtained from the following sources: sodium dodecyl sulfate (SDS – from Riedel de Haën), C_{12}–C_{14} alcohols polyoxyethyleneglycol ethers (7-EO) (Marlipal 24/70 – from the Sasol Co.), dodecanol polyoxyethyleneglycol ether (23-EO) (Brij-35 – from Caledon Laboratories, Ontario), polyoxyethanyl-1,2,3-propanetriol-1-octadecanoate-2-hexadecanoate (EO-20), ethoxylated α-mono-di-glyceride (EMDG) – from BASF Corp., Gurnee, Illinois, sucrose laurate (L-1695 – from Mitsubishi-Kasai Food Corp., Mie, Japan), polyoxyethanyl α-tocopher-6-yl sebacate (EO-13) (PTS – as 15% in H_2O), and dodecyltrimethylammonium bromide (DTAB) as well as cetyltrimethylammonium bromide (CTAB) – were purchased from the Sigma–Aldrich company.

2.3. Preparation of the catalyst: entrapment of $Pd(OAc)_2$ within hydrophobicitized sol–gel

Tetramethoxysilane (TMOS, 3.6 ml, 24.2 mmol) in MeOH (2.4 ml, 59.3 mmol) was hydrolyzed with triply distilled water (TDW, 2.0 ml, 111 mmol) by magnetically stirring the mixture at 20 °C for 10 min. Separately, the hydrophobic alkoxysilane monomer $R_nSi(OR')_{4-n}$ where R = alkyl or aryl; R′ = Me, Et; n = 1–3 (6.68 mmol) was hydrolyzed similarly by stirring with the respective carbinol (MeOH or EtOH, 73 mmol) and TDW (22 mmol). The solutions of the two hydrolyzed silicon compounds were mixed and stirred magnetically at room temperature for 10 min and added to a solution of $Pd(OAc)_2$ (30 mg, 0.134 mmol) in 4 ml of CH_2Cl_2. Magnetic stirring was continued as long as possible. Gelation was usually completed within 24 h at room temperature. The resulting gel was dried at 80 °C at 0.5 Torr for 24 h, then washed with warm CH_2Cl_2 (3 × 10 ml) and redried to obtain constant weight. The washing as well as the immobilized catalyst was subjected to ICP analyses and divided into two portions for the catalytic processes.

For comparative experiments, $Pd(OAc)_2$ was also entrapped within hydrophilic sol–gel free of the hydrophobic components.

2.4. Preparation of the microemulsions

A mixture of bromobenzene (**1**) and styrene (**2**) (1.34 mmol of each) was stirred magnetically for 20 min at 23 °C with TDW (89.3 wt.%), the respective surfactant (3.3 wt.%) and the co-surfactant *n*-PrOH (6.6 wt.%). The resulting microemulsions were visually clear.

2.5. General procedure for the Heck coupling reactions

To a magnetically stirred mixture of the above immobilized $Pd(OAc)_2$ (that contained 0.067 mmol palladium) was added the freshly prepared microemulsion of **1** and **2** (1.34 mmol of each of them) together with K_2CO_3 (0.28 g, 2 mmol). The reaction flask was then introduced into a thermostat preheated to the required temperature. After the needed length of time, the mixture was cooled to 20 °C and the sol–gel material was filtered off. The filtrate was separated into two phases by addition of NaCl (2 g). The solid used catalyst as well as the aqueous layer of the filtrate was extracted with ether (2 × 40 ml), and the extracts were analyzed for palladium by ICP. The extracts never contained more than 0.01 mg Pd. The combined organic layers were dried ($MgSO_4$) concentrated and analyzed by both GC and ^1H NMR and compared with authentic samples of *E*- and *Z*-stilbene (**3** and **4**, respectively). The used sol–gel entrapped catalyst which proved by TEM and XPS studies to contain Pd(0) nanoparticles was washed with water (2 × 10 ml), in order to remove remains of the surfactant, dried at 80 °C/0.5 Torr for 1 h and then washed and sonicated for 10 min with CH_2Cl_2 (3 × 30 ml) and redried to obtain constant weight. The dry catalyst was ready for use in the next run.

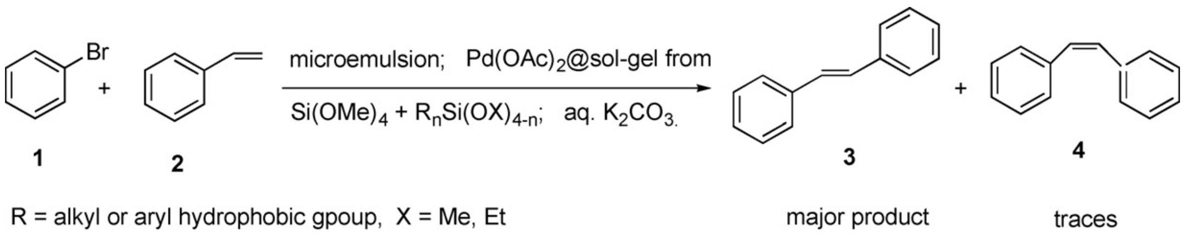
3. Results and discussion

3.1. Effect of the hydrophobicity of the sol–gel support

When a microemulsion of bromobenzene, styrene, sodium dodecyl sulfate and *n*-propanol was placed in a pressure vessel together with sol–gel material (prepared from prehydrolyzed tetramethoxylsilane, $Pd(OAc)_2$ and a solution of aqueous K_2CO_3), and the mixture was heated with stirring for 24 h at 80 °C, no coupling reaction took place. However, after replacement of ca. 5% of the TMOS by (octyltriethoxy)silane a quantitative yield of stilbenes (99% of the *E*- and 1% of the *Z*-isomer) was obtained already after 90 min at 66 °C. This observation led us to systematically study the effect of the hydrophobicity of the sol–gel support of the catalyst on the Heck coupling shown in Scheme 1.

Some representative results are listed in Table 1. In all experiments the main product (>97%) was the *E*-stilbene accompanied by traces of the *Z*-isomer (usually <1%). In none of the experiments has any 1,1-diphenylethene derivative been traced. The coupling processes proved to take place only above a threshold temperature below which hardly any reaction could be observed during the 90 min of the experiments. This temperature which extended over a very narrow limit of degrees was found to depend in the first place on the hydrophobicity of the sol–gel matrices in which the $Pd(OAc)_2$ pre-catalyst was entrapped. Table 1 indicates that in the series of experiments of alkyl functionalized sol–gel the threshold temperature decreases along with the increase of the hydrophobic-aliphatic chain length R (see entries 1 and 4–8). Multiple functionalization of the sol–gel (i.e., using monomers $R_nSi(OX)_{4-n}$ where n = 2 or 3 for the co-condensation with TMOS) further increases the hydrophobicity and decreases the threshold temperature (cf. entries 1–3). Comparison of the effect of aliphatic and aromatic hydrophobic groups, R, indicates the higher efficiency of the aromatic ones. (See also Ref. [21] for some analogous catalyses that take place within mesoporous silicates.) We assume that this phenomenon is associated with the ability of aromatic substrates to form π-interactions with the ceramic matrices which are stronger than the van-der-Waals forces that bind aliphatic groups to the support. Hence, the application of (diphenyldiethoxy)silane and (triphenylethoxy)silane used to prepare the supports in entries 10 and 11, respectively, gave the best results among the couplings studied. Entries 9, 12 and 13 reveal that the efficiencies of the immobilized catalyst depend also on the electronic nature of the hydrophobic groups R. Thus, a decrease in the threshold temperature (and an increase in the reactivity) was observed when the hydrophobicitization was introduced by the monomers (4-chlorophenyltriethoxy)silane < (phenyltriethoxy)silane < (4-tolyltrimethoxy)silane.

As shown previously [6] the used catalyst within octylated sol–gel is recyclable and can be applied at least in 4–6 consecu-



Scheme 1.

Table 1
Dependence of the formation of stilbenes on the hydrophobicity of the silica sol–gel support of the palladium acetate catalyst.[a].

Entry	R in Scheme 1	*n* in Scheme 1	Yield of stilbenes (%) at various temperatures (°C)[b,c]						
			50	55	60	63	66	70	75
1	CH_3	1	–	–	–	–	–	3	*q*[d]
2	CH_3	2	–	–	3	14	*q*		
3	CH_3	3	–	5	41	*q*			
4	C_2H_5	1	–	–	–	2	7	35	*q*
5	C_3H_7	1	–	–	–	1	*q*		
6	$(CH_3)_2CHCH_2$	1	–	–	1	16	32	*q*	
7	$CH_3(CH_2)_7$	1	–	–	1	4	*q*		
8	$CH_3(CH_2)_{17}$	1		5	9	*q*[e]			
9	C_6H_5[f]	1	3	6[g]	27	*q*			
10	C_6H_5[f]	2	13	26	*q*				
11	C_6H_5[f]	3	14	*q*[g]					
12	4-$C_6H_4CH_3$[f]	1	nd	nd	59	*q*			
13	4-C_6H_4Cl[f]	1	nd	nd	nd	nd		30	92[h]
14	1-$C_{10}H_7$[f]	1	nd	3	10	34		*q*	

[a] *Reaction conditions*: microemulsion of 1.34 mmol of **1** and 1.34 mmol of **2**, 5 mmol of SDS, 4.8 mmol of PrOH, 39 ml of H_2O, 2 mmol K_2CO_3, 0.067 mmol of $Pd(OAc)_2$ entrapped within sol–gel material from 24 mmol hydrolyzed TMOS and 7 mmol $R_nSi(OX)_{4-n}$ where X is either Me or Et; reaction time 90 min.

[b] The data refer to the first run.

[c] q = 96–100%; the missing percentage refers to unreacted starting materials. nd: not determined.

[d] 78 °C.

[e] Second run.

[f] 1-$C_{10}H_7$: 1-naphthyl. One milliliter of CH_2Cl_2 was added.

[g] 57 °C.

[h] After 3 h at 90 °C.

tive runs. We now find that the catalyst entrapped within the other hydrophobicitized sol–gels behave likewise.

3.2. Involvement of Pd nanoparticles in the reactions

The dependence of the yields of the coupling reactions on the hydrophobicity of the sol–gel matrices is notable. Since TEM analysis reveals that in *all* the experiments listed in Table 1 palladium nanoparticles are formed [22,23] we suggest that these particles interact with the differently hydrophobicitized silicates. Thus, differently modified catalysts may have been generated. We have shown that much of the sol–gel entrapped Pd(0) nanoparticles are obtained already during the entrapment of the $Pd(OAc)_2$ within the hydrophobic sol–gel material [22], but further active species are likely to be formed (as well as to be removed through aggregation) during the coupling process. Support for this assumption was obtained from some kinetic measurements of the formation of the stilbene shown in Scheme 1. The composition/time profiles shown in Fig. 1 clearly indicate an induction period in the first run during which some additional active catalyst may have been generated. In the second, and in further runs, this induction period disappears, probably because at this point the entire pre-catalyst has already turned into enough active species. After the induction period the formation of the stilbenes increases in a nearly linear fashion with time up to 80% conversion and slows down afterwards. This behavior can be explained considering that the rate determining step of the Heck coupling is the oxidative addition of the aryl halide to the palladium. During the linear course of the reaction the catalyst is completely saturated by the aryl halide and the reaction rate is nearly constant. At higher conversion the catalyst is no longer saturated and the reaction rate decreases. In Fig. 2 the rate/conversion profile for the second run of the stilbene formation is shown. The rates were calculated from an Eley–Rideal rate law fitted to the experimental conversions shown in Fig. 1.

An alternative explanation based on active palladium species leaching into the aqueous medium seems rather unlikely since ICP analysis found the entire palladium stays within the sol–gel mate-

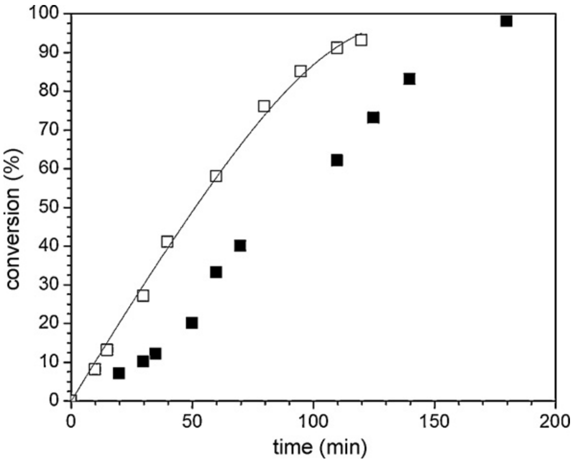


Fig. 1. Conversion/time profiles for the formation of stilbenes from **1** and **2** in water by $Pd(OAc)_2$ within octylated sol–gel under EST conditions in the first (■) and second (□) runs at 65 °C. The solid line was obtained from the Eley–Rideal rate law fit.

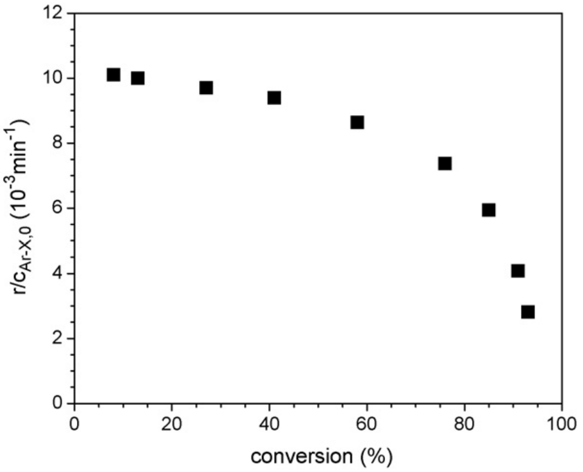


Fig. 2. Rate/conversion profile for the formation of stilbenes for the second run at 65 °C.

rial. No active palladium species could be traced in the filtered reaction mixture after the second run.

It is notable, that the coupling rate of **1** and **2** in toluene at 100 °C, by immobilized bis-palladium L-prolinate [22], which does not generate detectable Pd(0) nanoparticles, is hardly affected by changes in the hydrophobicity of the ceramic support. In fact, the coupling of **1** and **2** by the prolinate catalyst [24] in aromatic solvents (e.g., toluene) gives the best results in a hydrophilic sol–gel prepared from TMOS alone.

3.3. *Effect of the structure of the surfactant*

Apart from the effect of the hydrophobicity of the sol–gel support on the Heck coupling, we investigated the dependence of the reaction on the nature of the surfactant. When the anionic SDS, used in our initial experiments, was replaced by either the non-ionic polyethoxylated C_{12}–C_{14} alcohol (Marlipal 24/70) or by the cationic decyl- or cetyltrimethylammonium bromide, the coupling was accelerated. While the attempts to perform the coupling of **1** and **2** with an SDS based microemulsion of the reactants in the presence of hydrophilic sol–gel at 80 °C for 24 h, gave negative results (Table 2, entry 1), the replacement of this surfactant by the non-ionic or by the cationic ammonium bromides (entries 4, 9 and 10, respectively) initiated the formation of stilbene. Yet much better results were obtained by the application of hydrophobicitized sol–gel supports. Thus, e.g., in the presence of phenylated sol–gel, SDS, Marlipal 24/70 and CTAB yielded already after 1.5 h at 57 °C, 6, 14 and 28% of the desired products, respectively (Table 2, entries 3, 6 and 12). Since the EST process relies on the ability of the surfactant to transfer the substrates onto the immobilized catalyst, it is obvious that the catalytic process is affected by the adsorption capacity of the sol–gel matrix. Because of electronic reasons the anionic SDS is actually repelled by the negatively charged non-hydrophobicitized TMOS polymer. This effect is less pronounced by the non-ionic Marlipal 24/70 and actually reversed when the cationic surfactants are applied [21,25,26]. Working with a microporous sol–gel material that enables the recycling of the catalyst, one should also take into consideration that EST conditions are limited to surfactant micelles (and substrates) that are capable of penetrating freely the pores of the ceramic material. The initial average pore diameters of the octylated and phenylated sol–gel supports were determined by BET measurements [6] to be 31.5 and 28 Å, respectively. Thus, while the surfactant micelles with relatively small sizes shown in Table 3 can be applied in the Heck coupling under EST conditions, larger ones proved useless. While Marlipal 24/70, e.g., is quite effective with conversions of 14–15%, the closely related, but more voluminous ethoxylated α-mono-di-glyceride (EMDG) micelles, do not lead to any stilbenes even if the reaction temperature is raised to 90 °C (cf. a similar size effect of the substrates on the disproportionation of hydroaromatics by sol–gel entrapped $RhCl_3 \cdot R_4N$ [27]). Also, the commercially available polyoxyethanyl α-tocopher-6-yl sebacate (PTS) surfactant which promotes the Heck and other coupling reactions at room temperature in sol–gel free systems [8], cannot be applied to our process under the EST conditions. The sizes of the active surfactant micelles (without the substrates) have been determined by dynamic light scattering (DLS). The fact that their diameters increase in the following order: SDS < CTAB < Brii 35 < Marlipal 24/70 reveals that the size of the micelles is not the only factor that has an effect on the yields disclosed in Table 2.

Table 2
Dependence of the coupling of bromobenzene and styrene under the EST conditions on the surfactants.[a]

Entry	Surfactant[b]	Lipophilic function	Reaction temperature (°C)	Yield after 1.5 h (%)
1	SDS	None	80	0[c]
2	SDS	$CH_3(CH_2)_7$	63	4
3	SDS	C_6H_5	57	6
4	Marlipal 24/70	None	80	2
5	Marlipal 24/70	$CH_3(CH_2)_7$	63	15
6	Marlipal 24/70	C_6H_5	57	14
7	Brij-35	C_6H_5	57	8
8	L1695	C_6H_5	57	5
9	DTAB	None	80	12
10	CTAB	None	80	9
11	CTAB	$CH_3(CH_2)_7$	63	18
12	CTAB	C_6H_5	57	28

[a] *Reaction conditions*: microemulsion of 1.34 mmol of each of **1** and **2**, 1.42 g of surfactant, 2.84 g PrOH, 38.5 g TDW, 15 mg $Pd(OAc)_2$ entrapped within sol–gel from 24.2 mmol of TMOS and 6.68 mmol of the hydrophobic monomer $R_nSi(OR')_{4-n}$; heating with stirring for 1.5 h.

[b] For the structures and sources of the surfactants see Section 2. The inactive surfactants EMDG and PTS have not been incorporated in the table.

[c] After 24 h.

Table 3
Sizes of some surfactant micelles determined by dynamic light scattering (DLS).[a].

Entry	Surfactant	$d_{micelle}$ (nm)
1	SDS	2.1
2	Marlipal 24/70	12.8
3	Brij-35	7.9
4	CTAB	5.4

[a] The setup for the determination of the micelle sizes consisted of a 1 W Nd:YAG laser and an ALV 5000/E autocorrelator. The analysis of the recorded correction functions was done by the comulant method.

4. Conclusions

Palladium acetate-catalyzed Heck coupling of bromobenzene and styrene under microemulsion/sol–gel transport conditions in aqueous media depends both on the hydrophobicity of the sol–gel material, as well as on the electronic nature of the surfactant micelles. Hydrophobicitation of the ceramic support by phenyl moieties is superior to that by aliphatic groups. The $Pd(OAc)_2$ decomposes during its immobilization and during the catalytic coupling into sol–gel stabilized Pd(0) nanoparticles. The latter are assumed to react with the various hydrophobicitizing additives. Cationic and non-ionic surfactants are more efficient than anionic ones. The surfactant micelles must be small enough to be able to freely penetrate the pores of the sol–gel within which the catalyst is entrapped.

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