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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@SiO_2 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.

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 $PdCl_2$-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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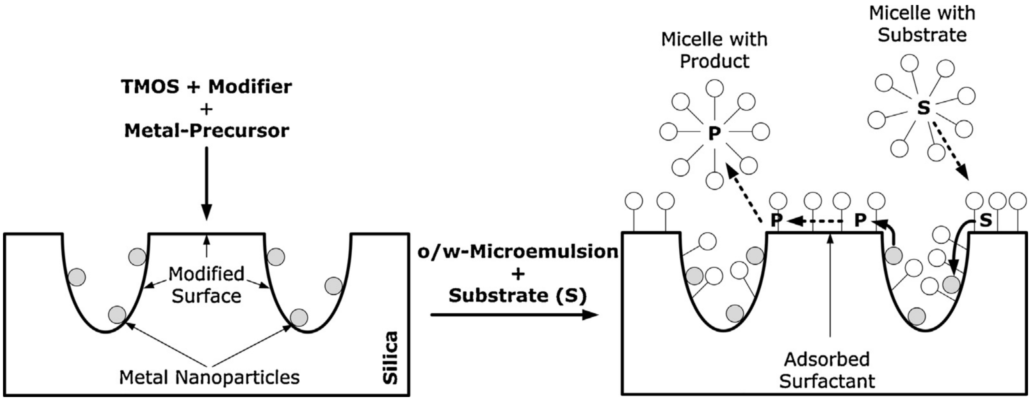

Scheme 1. Mechanism of the sol–gel supported catalysis in microemulsion as reaction medium.

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@SiO$_2$, 5 wt% Pd) and palladium(II) bromide (PdBr$_2$) 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$^{®}$35) and palladium on activated carbon (Pd@C, 10 wt% Pd) were ordered from *Merck KGaA* Darmstadt/Germany. Acetonitril (ACN), dimethyl formamide (DMF) and water (HPLC grade) were purchased from *Carl Roth GmbH & Co. KG* Karlsruhe/Germany. Marlipal 24/60 was provided from *Sasol Germany GmbH* Marl/Germany. α-Methylstyrene, 4-bromoacetophenone, bromobenzene (PhBr), 4-bromobenzylamine, 1-bromo-4-iodobenzene (IPhBr), *tert*-butylmethacrylate, 4-chloroacetophenone, chlorobenzene (PhCl), 2-chloro-benzonitrile, 2-chloro-1,3-dimethylbenzene, 1-chloro-2-nitrobenzene, 4-chlorostyrene, *trans*-4-chlorostilbene, dodecyltrimethylammonium bromide (DTAB), hexadecyltrimethylammonium bromide (CTAB), 2-hydroxyethylmethacrylate, IGEPAL CA-520, iodobenzene (PhI), palladium (1000 mg/L) and phosphor (1000 mg/L) ICP standard solutions, methacrylic acid, methylacrylate, α-methylcinnamic acid, methylmethacrylate, methyl-α-methyl-cinnamate, palladium on alumina powder (Pd@Al$_2$O$_3$, 1 wt%), palladium(II) acetate (Pd(OAc)$_2$), poly(4-vinylpyridine) (PvyPy), potassium carbonate (K$_2$CO$_3$), tetramethyl orthosilicate (TMOS), *trans*-stilbene, triethoxyphenylsilane (PhSi(OEt)$_3$), trimethoxy(octyl)-silane (OcSi(OMe)$_3$), dioctyl sodium sulfosuccinate (DSS), Triton X-100 (TX-100) and 4,5-bis(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 °C and then it was dried for another 8–10 h at 80 °C and 10^3 Pa to remove the solvents. The catalyst was washed carefully with boiling dichloromethane and dried again at 80 °C and 10^3 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 μL