



Short Communication

Sol-gel immobilized catalyst systems for tandem transformations with *trans*-stilbene as an intermediateI. Volovych^a, M. Schwarze^{a,*}, Z. Nairoukh^b, J. Blum^b, M. Fanun^c, R. Schomäcker^a^a Institute of Chemistry, Berlin Institute of Technology, Straße des 17. Juni 124, D-10623 Berlin, Germany^b Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel^c Center for Colloid and Surface Research, Al-Quds University, East Jerusalem 51000, Palestinian Authority

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ABSTRACT

Tandem catalytic systems containing one or two sol-gel immobilized catalysts were successfully applied in the synthesis of *trans*-stilbene oxide and 1,2-diphenylethane. The catalysts were prepared from palladium and/or manganese precursors in the presence of orthosilicates using a sol-gel method and could be reused several times successfully.

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1. Introduction

One of the recent trends in modern chemical process research is the development of greener processes. Paul Anastas formulated some simple rules about achieving sustainability in the production of chemicals, e.g. avoiding waste, working with high atom efficiency, usage of catalysts and renewable feed stocks. In this case more environmentally friendly processes can be realized by reusing solvents, catalysts and organic components after each reaction which reduces the costs and the environmental impact of the process by applying green solvents (e.g., water) in the synthesis of the desired products.

In the course of our work, we developed and tested green reaction routes with *trans*-stilbene as an intermediate (Scheme 1), which is an important component in pharmaceuticals and fine chemicals, e.g. Herbicide ProsulfuronTM, antiasthma agent SingulairTM, analgesic drug Naproxen [1], anticancer agent Paclitaxel (Taxol[®]) [2], stilbenoid resveratrol with anti-tumor properties and optically active distyrylbenzene or styrylbiphenyl [3], which can be used as fluorescent dopants in organic light emitting diodes and lasers.

Two different tandem reactions were selected: the synthesis of *trans*-stilbene using Heck coupling followed by hydrogenation to 1,2-diphenylethane and epoxidation to *trans*-stilbene oxide. Following the concepts of green chemistry, the conventional organic solvents

were replaced by more environmentally friendly media, namely aqueous microemulsions. Supported palladium, manganese and palladium-manganese catalysts synthesized by using a sol-gel method were used in the process to improve catalyst recycling. The general mechanism of the sol-gel process is known, but the influence of immobilization on different metals in the silica matrix was studied only for selected examples [4–7]. In this case, we tried to determine the parameters that influence the activity and stability of sol-gel-immobilized catalysts and compare their performance.

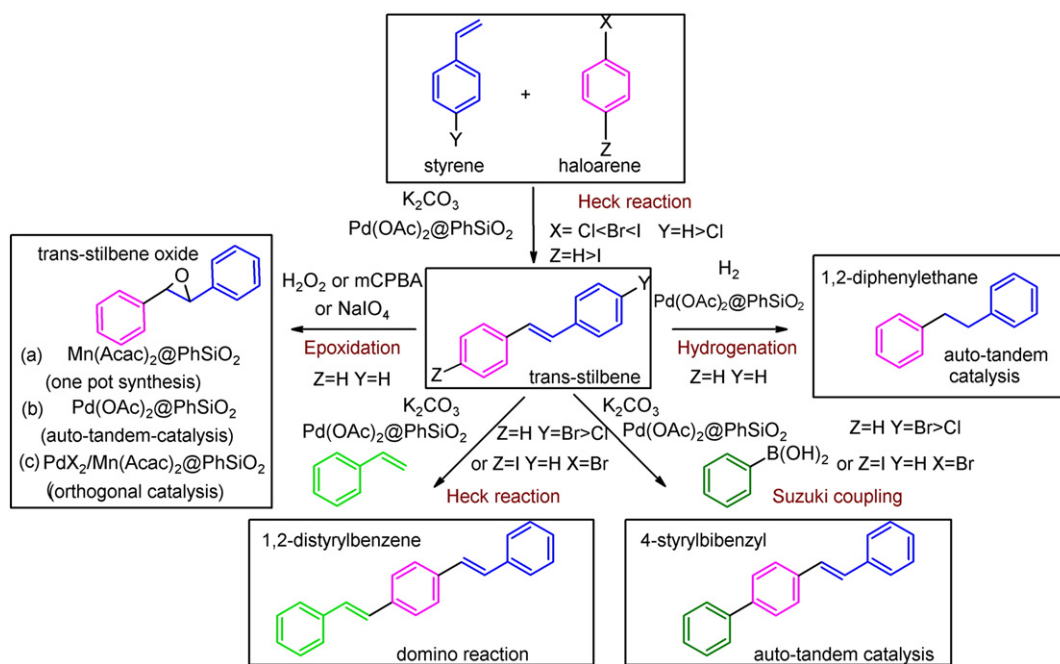
2. Experimental

2.1. Instrumentation

All reagents were commercially available and used without further purification. The conversion (X) and yield (Y) were obtained using high performance liquid chromatography (HPLC) on an Agilent instrument 1200 series from Agilent Technologies Waldbronn/Germany with 250 × 4 mm chromatographic column Multospher 120 RP18-5 μ m from Ziemer Chromatographie Langerwehe/Germany. N₂-BET specific surface areas, pore volumes and pore size distributions were obtained using a Micromeritics Gemini 1325 instrument from Micromeritics GmbH Aachen/Germany. The amounts of palladium, manganese and phosphorus leached from the catalysts into the reaction mixtures were analyzed using a Varian 715-ES Optical Emission Spectrometer from Varian Inc. Middelburg/Netherlands.

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Scheme 1. Tandem reactions.

2.2. Catalyst synthesis

For the preparation of the catalysts on a hydrophobically modified surface, a solution of 2.1 mL of trimethoxy(octyl)silane (9.877 mmol) or 1.612 mL triethoxyphenylsilane (6.680 mmol) in 0.4 mL water and 4.25 mL methanol or ethanol was hydrolyzed for 24 h. Then, 3.6 mL of tetramethyl orthosilicate (22.961 mmol) in 2.4 mL of methanol and 2 mL of water was stirred for 20 min. The solutions were combined and stirred for another 30 min. Then, 30 mg of palladium(II) acetate, 35 mg of palladium(II) bromide, 33 mg of manganese(II) acetylacetonate (0.134 mmol) or a mixture of palladium(II) bromide and manganese(II) acetylacetonate catalyst precursor with/without 30.420 mg of XantPhos (0.134 mmol) or 1.24 g of 30% TPPTS/H₂O (0.640 mmol) ligand were dissolved in 4 mL of dichloromethane, stirred for 20 min (12 h with ligand) and combined with the silane solution and stirred until gelation occurred. The hydrophilically modified immobilized palladium (II) acetate catalyst was prepared without the addition of hydrophobic silane to the hydrolyzed tetramethyl orthosilicate. The catalyst was dried for 4–8 h at 80 °C followed by drying for 8–12 h at 80 °C and 10³ Pa, washing with dichloromethane and drying at 80 °C and 10³ Pa for 8–10 h. Finally, 1.25 wt.% Pd(OAc)₂ with/without ligand on silica support, 1.47 wt.% Mn(Acac)₂ or 1.06 wt.% Pd(OAc)₂/1.20 wt.% Mn(Acac)₂ with/without ligand on PhSiO₂ were obtained.

Table 1
Optimization of reaction conditions in the synthesis of *trans*-stilbene.^a

Entry	Catalyst	Support	Surfactant	Time (min)	Yield (%)
1	Pd(OAc) ₂	PhSiO ₂	CTAB	396	96
2	PdBr ₂	PhSiO ₂	CTAB	386	66
3	Pd(OAc) ₂ /Xantphos	PhSiO ₂	CTAB	352	74
4	Pd(OAc) ₂ /TPPTS	PhSiO ₂	CTAB	416	73
5	Pd(OAc) ₂	SiO ₂	CTAB	394	60
6	Pd(OAc) ₂	OcSiO ₂	CTAB	300	81
7	Pd(OAc) ₂	PhSiO ₂	TTAB	405	54
8	Pd(OAc) ₂	PhSiO ₂	DTAB	371	58
9	Pd(OAc) ₂	PhSiO ₂	SDS	380	96
10	Pd(OAc) ₂	PhSiO ₂	TX-100	388	92

^a 1.34 mmol styrene, 1.5 mmol bromobenzene, 2 mmol K₂CO₃, 1.25 wt.% Pd(OAc)₂@silica support, 46 mL microemulsion, 80 °C.

2.3. Reaction procedure

The Heck coupling, epoxidation and tandem reactions were performed in a double-walled, stirred glass reactor with a reflux condenser. The hydrogenation reactions were performed in 100 mL of methanol or an aqueous microemulsion at an 800 rpm stirring rate and 1.1 × 10⁵ Pa H₂ in a stirred tank reactor. The cumulative hydrogen consumption and the pressure during the reaction were measured using a Bronkhorst flow meter and pressure controller (Bronkhorst Mättig GmbH, Kamen/Germany) and recorded on a PC. From these results the substrate concentration *c*_{substrate} and the conversion *X* were calculated. All reactions were conducted in one phase aqueous microemulsions, consisting of 1.510 g CTAB as the surfactant (5.235 mmol, 3.3 wt.%), 3.020 g 1-propanol (50.250 mmol, 6.6 wt.%) as the cosurfactant, 40.855 g of H₂O (2269.722 mmol, 89.3 wt.%) and reactants (2.84 mmol, 0.8 wt.%).

For Heck coupling, 1.34 mmol alkene and 1.50 mmol aryl halide were dissolved in a 46 mL microemulsion with 0.276 g K₂CO₃ (2.00 mmol)

Table 2
Trans-stilbene synthesis via Heck coupling.^a

Entry	W	X	Y	Time (min)	Yield (%)
1	H	Cl	H	327	62
2	H	Br	H	555	100
3	H	I	H	480	94
4	H	Br	I	398	89 ^b
5	Cl	Br	H	371	50 ^c
6	Cl	I	H	415	92 ^c
7	H	Cl	styrene	419	0 ^d
8	H	Br	styrene	448	20 ^d

^a 1.34 mmol styrene, 1.5 mmol haloarene, 2 mmol K₂CO₃, 1.25 wt.% Pd(OAc)₂@PhSiO₂, 46 mL microemulsion, 80 °C.

^b 4-*trans*-bromostilbene.

^c 4-*trans*-chlorostilbene.

^d Tandem Heck–Heck domino reaction.

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