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Catalytic transfer hydrogenation of hydrophobic substrates by water-insoluble hydrogen donors in aqueous microemulsions

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ABSTRACT

In the course of our attempts to replace harmful organic solvents used in organic processes by environmentally favored media, we investigated the transfer hydrogenation of various, unsaturated substrates by cyclohexene and similar water-insoluble hydrogen donors. The catalyst in these reactions was Pd(0) in form of nanoparticles, stabilized by hydrophobic silica sol–gel which can be reused at least 4–6 times without significant loss of activity. The process was shown to depend on the electronic nature of the surfactants. Marlipal® 24/70 gave in most experiments the best results. Except for the hydrolysable 1-chloromethylnaphthalene, where chlorine can be substituted by a hydroxyl group, the aqueous medium does not take part in the catalytic process.

1. Introduction

Transfer hydrogenation of unsaturated compounds is a “green” version of the conventional hydrogenation. It may avoid the danger associated with the transport of hydrogen in cylinders [1]. When the hydrogen donors (such as alcohols or formic acid derivatives) as well as the unsaturated acceptors are water-soluble, the reactions can be conducted in aqueous media [2] (see also the comprehensive monographs on organic synthesis in water [3,4]). When however, the reaction components are water-insoluble, most industrial plants prefer the application of organic media. In the course of our attempts to replace as much as possible of the large quantities of the harmful solvents by environmentally favored aqueous media, we have already shown that the use of either aqueous emulsions [5] or microemulsions [6] obtained in the presence of micelle-forming surfactants, enables the performance of a variety of organic catalyses in aqueous media even if all the reaction components are water insoluble [7–10]. The use of sol–gel entrapped pre-catalysts gives emulsion/sol–gel transport systems (EST) [6] applicable to some different hydrogen transfer processes and to C–C couplings of water-insoluble substrates. We now find that in the presence of the palladium acetate pre-catalyst the EST system is also applicable to catalytic transfer hydrogenation reactions of a variety of lipophilic acceptors from water insoluble donors. The reactions shown in Schemes 1-6a were usually very efficient. Except for a few exceptions, the turnover frequencies (TOF) were between 100 and 5200 h^{-1}. The turnover numbers (TON) extended under our conditions to 1300 and the catalyst could be recycled easily.

In the absence of a surfactant the formation of the microemulsions did not take place (checked by the laser light scattering analysis) and consequently the heterogenized catalyst failed to promote any transfer hydrogenation.

2. Experimental

2.1. Instruments

NMR spectra were recorded with either a Bruker DRX-400 or a Bruker Avance II 500 in $CDCl_3$. Infrared spectra were obtained with a Perkin-Elmer 65 FTIR spectrometer. Mass spectral measurements were performed with a Q-TOF-II spectrometer. ICP-MS analyses were carried out with a Perkin-Elmer model Elan DRC II instrument. Gas chromatographic separations and analyses were carried out on a Hewlett Packard model Agilent 4890D equipped with either a 30 m long column packed with Carbowax 20 M-poly(ethylene glycol) in fused silica (Supelco 25301-U) or with a 15 m long column

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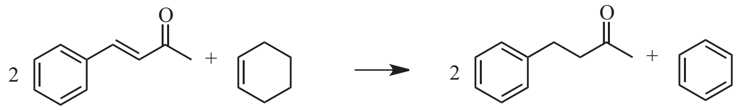
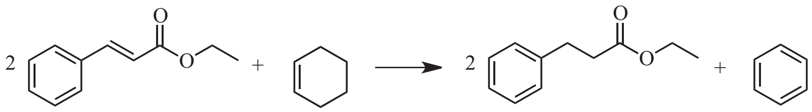
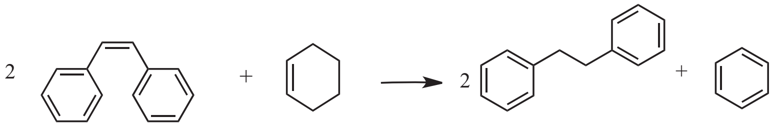


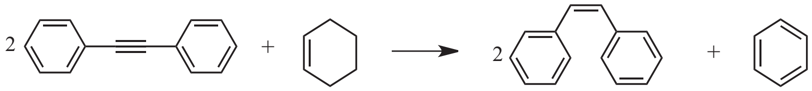
Scheme 1. Transfer hydrogenation of benzylidene acetone.



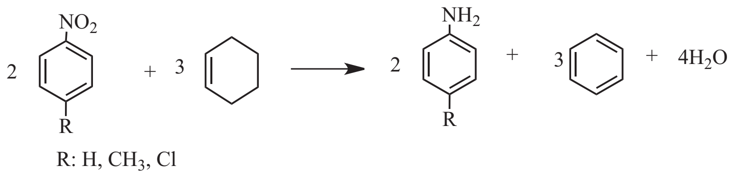
Scheme 2. Transfer hydrogenation of ethyl cinnamate.



Scheme 3. Transfer hydrogenation of (*Z*)-stilbene.



Scheme 4. Transfer hydrogenation of diphenylacetylene.



Scheme 5. Transfer hydrogenation of some nitrobenzene derivatives.

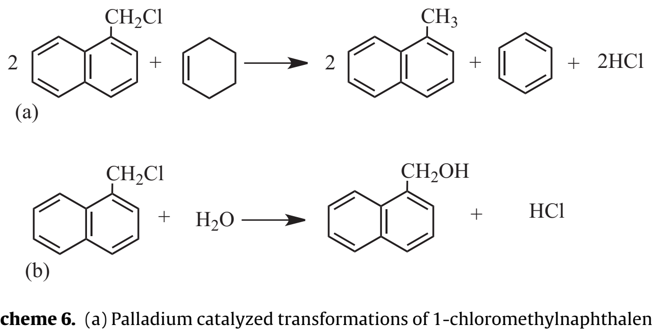
packed with a bonded crosslinked (5% phenyl) methylpolysiloxane [HP-5]. XPS measurements were performed with a Kratos Axis ultra X-ray photoelectron spectrometer. The spectra were acquired with monochromated AlKα (1486.7 eV) X-ray source with 0° take off angle. The pressure in the test chamber was maintained at 1.5×10^{-9} Torr during the acquisition process. High resolution XPS scans were collected for Pd 3d and C 1s peaks with pass energy of 20 eV. The XPS binding energy was calibrated with respect to the peak position of C 1s as 285.0 eV. Data analysis was performed with Vision processing data reduction software (Kratos Analytica Ltd. and Casa SPX Software Ltd.). Transmission electron microscopy (TEM) was done with a Scanning Transmission Electron Microscope Technai G^2 F20 (FEI Company, USA) operated at 200 kV and equipped with an EDAX-EDS device for identification of the elemental composition. Initial powders were dispersed in ethanol and dropped onto a standard 400 mesh carbon coated copper TEM grid.

2.2. Chemicals

All the substrates and reference compounds, as well as palladium acetate, cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium bromide (DTAB) were purchased from the Sigma–Aldrich Company. Tetramethoxysilane (TMOS), propyltrimethoxysilane (PTMOS), octyltriethoxysilane (OTEOS) and phenyltriethoxysilane (PhTEOS) were obtained from ABCR (Glest, Inc.). Sodium dodecyl sulfate (SDS) was purchased from Riedel de Haën. C_{12}–C_{14} alcohols polyoxyethyleneglycol ethers (7-EO-Marlipal 24/70) was obtained from the Sasol Company.

2.3. Preparation of the heterogenized palladium catalyst

Typically, the alkoxysilane $RSi(OR^1)_3$, where $R = n\text{-}C_3H_7$ or $n\text{-}C_8H_{17}$ and R^1 = Et or Me (6.68 mmol), was hydrolyzed by stirring with a mixture of EtOH (73 mmol) and triply distilled water (TDW, 22 mmol) for 24 h. Separately TMOS (3.6 ml, 24.2 mmol) was hydrolyzed with TDW (2.0 ml) by stirring for 10 min. The solutions of the two hydrolyzed silicon compounds were united and stirred magnetically for 10 min at 25 °C and added to a solution of $Pd(OAc)_2$ (30 mg, 0.134 mmol in 4 ml CH_2Cl_2). The stirring was



Scheme 6. (a) Palladium catalyzed transformations of 1-chloromethylnaphthalene in aqueous microemulsion by cyclohexene. (b) Hydrolysis of 1-chloromethylnaphthalene in the aqueous medium.