



# Synthesis and catalytic evaluation in the Heck reaction of deposited palladium catalysts immobilized via amide linkers and their molecular analogues



Miloslav Semler<sup>a,b</sup>, Jiří Čejka<sup>b</sup>, Petr Štěpnička<sup>a,\*</sup>

<sup>a</sup> Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, 128 40 Prague, Czech Republic

<sup>b</sup> J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 182 23 Prague, Czech Republic

## ARTICLE INFO

### Article history:

Received 21 June 2013

Received in revised form

11 September 2013

Accepted 17 September 2013

Available online 12 October 2013

### Keywords:

Deposited catalysts

Palladium

Amide linkers

Heck reaction

Poisoning tests

## ABSTRACT

A series of deposited palladium catalysts was prepared by amidation of 3-aminopropylated silica gel with donor-functionalized acetic acids followed by treatment with palladium(II) acetate. The resulting materials containing  $\text{YCH}_2\text{CONH}(\text{CH}_2)_3\text{Si}\equiv$  groups at the surface, where  $\text{Y} = \text{SMe}$ ,  $\text{NMe}_2$ , and  $\text{PPh}_2$ , as well as the corresponding catalysts generated in situ from the analogous molecular donors  $\text{YCH}_2\text{CONH}(\text{CH}_2)_2\text{Me}$  and palladium(II) acetate were evaluated in the Heck reaction of *n*-butyl acrylate with bromobenzene to give *n*-butyl cinnamate. The heterogenized catalysts afforded consistently better yields of the coupling product than their respective molecular counterparts with the best results being achieved with the catalyst obtained from the amidoamine-functionalized support ( $\text{Y} = \text{NMe}_2$ ). Additional tests revealed that the deposited catalysts serve as a source of active metal for the reaction occurring in the liquid phase and that the yield of the coupling product is controlled by the amount of the leached-out metal.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Catalysis nowadays plays a vital role in the synthesis of many organic compounds at laboratory scale as well as in industry, where not only fine chemicals but also large scale preparations are carried out catalytically. Very often, high value added chemicals are prepared with the aid of C–C bond forming (cross-coupling) reactions that allow for efficient “construction” of a range of simple and complex molecules by selective coupling of two building blocks via the newly formed C–C bond(s). One of the prominent examples of such processes is the Heck–Mizoroki reaction (or simply Heck reaction) discovered in the early 1970s [1]. Heck reaction is based on the coupling of olefins with organic halides (typically haloarenes) affording substituted alkenes suitable for further synthetic transformations [2]. The manifold industrial applications of Heck reaction, which have been reviewed several times [3], can be exemplified by the preparation of materials as diverse as monomer precursors of benzocyclobutene-based resins (Cyclotene™ by Dow Chemical), herbicide Prosuluron, and the nonsteroidal anti-inflammatory drug Naproxene.

Typically, the Heck reactions make use of various palladium catalysts ranging from defined molecular compounds (i.e., various Pd

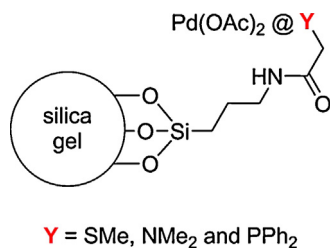
salts and complexes) and “molecular” catalysts generated in situ from a Pd precursor and an appropriate modifier (typically a ligand), to various heterogeneous and heterogenized catalysts. Any immobilization of a palladium catalyst over a solid support is potentially attractive for industrial, large-scale applications because such catalysts can be relatively easily recovered and recycled. In addition, the stable and efficient heterogenized catalysts appear particularly suitable for the preparation of pharmaceutically active substances, in the case of which the contamination with residual metals is strictly controlled [4].

In our work, we have focused on palladium catalysts deposited on various siliceous supports modified with N-donor groups and their applications to the Heck coupling [5]. The results obtained with the catalysts derived from siliceous supports such as mesoporous molecular sieves MCM-41 [6] and SBA-15 [7] or much cheaper and hydrolytically stable silica gel have shown that the type (internal structure in particular) of the support affects the overall catalytic performance of the resulting immobilized catalysts less than the amount and the nature of the anchoring donor groups used to modify the parent support [5]. This is rather natural because the donor groups determine the mode of interaction between the deposited metal and the support, thereby controlling the activity, selectivity and stability of the catalyst, as well as a possible leaching of the active metal from the solid support.

Although a number of papers has been published on the applications of palladium catalysts deposited over siliceous supports

\* Corresponding author. Fax: +420 221 951 253.

E-mail address: [stepnic@natur.cuni.cz](mailto:stepnic@natur.cuni.cz) (P. Štěpnička).



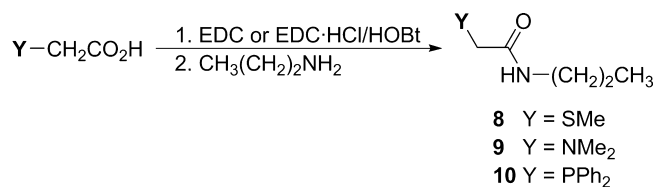
Scheme 1.

modified with aminopropyl [8], mercaptopropyl [9], phosphine [10] and carbene [11] donor groups in the Heck reactions, there is – up to the best of our knowledge – no literature report dealing with the direct comparison of catalysts possessing structurally similar modifying groups equipped with chemically different donor moieties. This prompted us to prepare a series of structurally analogous palladium catalysts from donor-modified, silica gel-based supports and to compare their catalytic properties in a model Heck reaction. To this end, we have synthesized palladium catalysts from silica gel functionalized with chemically similar amide donor pendant groups possessing different terminal donor moieties (Scheme 1). In the preparation of these materials, we used the readily accessible 3-aminopropyl modified silica gel, which was reacted with donor-functionalized acetic acids (Me<sub>2</sub>NCH<sub>2</sub>CO<sub>2</sub>H, Ph<sub>2</sub>PCH<sub>2</sub>CO<sub>2</sub>H, and MeSCH<sub>2</sub>CO<sub>2</sub>H) to afford the respective surface-bound amide pendants. This approach exploiting amide functional group as a defined linking moiety has been utilized only scarcely in the design of deposited palladium catalysts [12]. In this contribution, we report the preparation of deposited palladium catalysts from supports bearing three different donor-amide groups at the surface, and a comparison of their catalytic performance with simple catalysts obtained *in situ* by mixing a palladium source with the respective “molecular” donor-amide ligands.

## 2. Results and discussion

### 2.1. Preparation of the deposited catalysts and their molecular analogues

The deposited, donor-amide functionalized palladium catalysts were prepared as shown in Scheme 2 [13]. In the first step, dry chromatography-grade silica gel was reacted with an excess of (3-aminopropyl)trimethoxysilane in refluxing toluene to afford the aminopropylated support **1**. This material was in turn reacted with the respective substituted acetic acids in the presence of peptide coupling agents [14] to give the corresponding amide-functionalized supports **2–4**. As the last step, the supports were palladated via treatment with palladium(II) acetate in dichloromethane using 1 mmol of Pd(OAc)<sub>2</sub> per 1 g of the functionalized silica gel to afford catalysts **5–7**. Amides **8–10**, representing molecular analogues of the functional pendants present



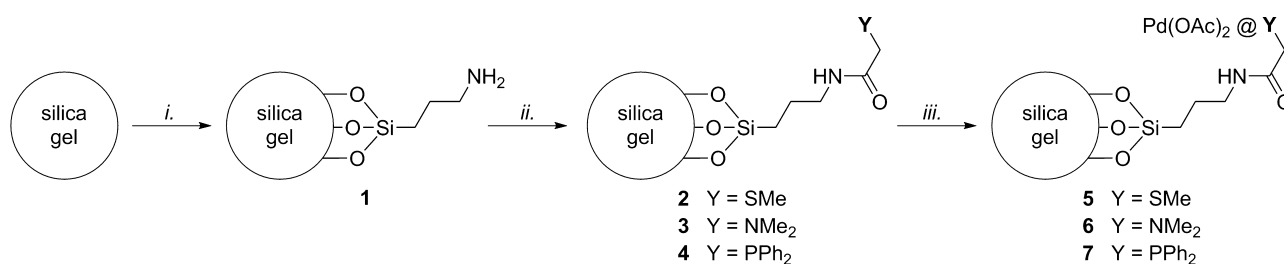
**Scheme 3.** Preparation of the molecular donors **8–10**. Legend: EDC, 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide; HOBt, 1-hydroxybenzotriazole.

in the deposited catalysts **5–7**, were obtained by direct amidation of the respective substituted acetic acids with 1-aminopropane (Scheme 3).

Materials **1–7** were characterized by IR spectroscopy and elemental analysis. Prior to the palladation, supports **2** and **4** showed the S/N and P/N molar ratios below unity while in the case of **3**, the amount of nitrogen was lower than the double of the amount of nitrogen in the parent material **1**. This suggests an incomplete conversion of the 3-aminopropyl pendants into the amide ones or, in other words, the presence of unreacted aminopropyl groups at the supports' surface [15]. The palladation led to incorporation of ca. 0.5–0.6 mmol Pd per gram of the resulting solid catalyst. The Pd/donor molar ratios were 1.06 (Pd/S) for **5** and 1.30 (Pd/P) for **7**. The Pd/N ratio determined for **6** was only 0.88 owing to the presence of two nitrogen atoms in the functional pendant (in the ideal case).

The IR spectra of all materials were dominated by broad intense absorptions of the siliceous support at 3000–3500 ( $\nu_{\text{OH}}$ ), ca. 1100–1200 cm<sup>-1</sup> (intense band due to asymmetric Si–O–Si stretching), 800 cm<sup>-1</sup> (symmetric Si–O–Si stretching), and 460 cm<sup>-1</sup> (Si–O–Si bending) [16]. Besides, the spectra of **2–4** displayed bands attributable to N–H vibrations, C–H valence bands (ca. 2750–3000 cm<sup>-1</sup>) and, mainly, characteristic vibrations of the amide moieties (amide I at 1640–1660 cm<sup>-1</sup>, and amide II at ca. 1535–1540 cm<sup>-1</sup>). The positions of the amide bands corresponded well with those determined for the respective molecular amides **8–10** (see below). Upon palladation, however, these bands shifted to lower wavenumbers (amide I band typically by ca. 90 cm<sup>-1</sup>), reflecting very likely coordination of the anchored Pd species by the donor pendant attached to the support surface. These features are demonstrated in Fig. 1 for materials obtained from *N,N*-dimethylglycine. Trends observed in the other series (i.e., **2–5–8** and **4–7–10**) were similar.

The molecular amides **8–10** were characterized by NMR and IR spectroscopy and by high-resolution mass spectrometry. The compounds displayed all expected signals in the NMR spectra as well as the characteristic amide bands at 1630–1650 (amide I) and 1530–1545 cm<sup>-1</sup> (amide II) in their IR spectra. Notably, the energy of the amide I vibration (largely C=O stretching) was found to increase in the order **10** < **8** < **9** (P < S < N), thus following inversely the trend of the electronegativities of the pivotal atoms in the terminal group (N > S > P).



**Scheme 2.** Preparation of anchored Pd catalysts **5–7**. Legend: *i*, (3-aminopropyl)trimethoxysilane in toluene, refluxing; *ii*, amidation with the appropriate acid YCH<sub>2</sub>CO<sub>2</sub>H in the presence of peptide coupling agents (1-hydroxybenzotriazole and 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide (EDC) or the corresponding hydrochloride (EDC-HCl)); *iii*, treatment with Pd(OAc)<sub>2</sub> in dichloromethane.

Download English Version:

<https://daneshyari.com/en/article/54177>

Download Persian Version:

<https://daneshyari.com/article/54177>

[Daneshyari.com](https://daneshyari.com)