

# Anchoring of Pd on silica functionalized with nitrogen containing chelating groups and applications in catalysis

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Received 2 July 2001; accepted 22 October 2001

## Abstract

Pd-complexes of silica-anchored nitrogen containing chelating compounds were prepared by the following reactions: (a) synthesis of the Schiff-bases from 3-aminopropyltriethoxysilane and 2-acetylpyridine, 2-acetylpyrazine or 2,6-diacetylpyridine; (b) reduction of the Schiff-bases with NaBH<sub>4</sub> in methanol; (c) cogelification with tetraethyl orthosilicate (TEOS); (d) reaction of the obtained functionalized silica with [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub>. The corresponding model ligands and palladium complexes were also prepared from the reaction of *n*-propylamine with the pyridine or pyrazine compound, followed by the reduction with NaBH<sub>4</sub> and the reaction with [PdCl<sub>2</sub>(PhCN)<sub>2</sub>]. The products were characterized by BET, FTIR, GC-MS, <sup>1</sup>H-NMR and elemental C–H–N analysis. The anchored Pd-complexes were tested as catalysts in: (a) the Heck reaction of iodobenzene with ethyl acrylate or styrene in the presence of tributylamine, as base, and toluene or *p*-xylene, as solvent; (b) the carbonylation reaction of iodobenzene with CO, at atmospheric pressure, in methanol in the presence of triethylamine or potassium acetate, as base. The catalysts were separated from the reaction mixtures and re-used many times. The best results were obtained in both reactions with the anchored Pd-complexes prepared from 2-acetylpyridine: 14 cycles in the Heck reaction (TON ≈ 4100 mmol product/mmol Pd) and 20 cycles in the carbonylation of iodobenzene (TON ≈ 2300 mmol product/mmol Pd). © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Silica-anchored palladium; Schiff-bases; Heck arylation; Carbonylation; Methyl benzoate

## 1. Introduction

The use of heterogeneous catalysts for commonly homogeneously catalyzed organic reactions may help to resolve some industrially important problems, such as the recovery of the catalyst from the reaction mixture and its re-use in order to lower production costs. Palladium-based homogeneous catalysts are very active and selective in industrial organic syntheses [1] to make a wide range of important products like aryl

acids, aldehydes, esters or amides. The Heck reaction between aryl halides and alkenes [2,3], or the carbonylation of aryl halides with carbon monoxide and alcohols [4], are significant examples of carbon–carbon bond forming reactions, using palladium homogeneous catalysts, whose industrial importance is well-known. The use of palladium metal catalysts in Heck C–C coupling reactions has been very recently overviewed [5]. As well as conventional catalysts, e.g. Pd–C and Pd–Al<sub>2</sub>O<sub>3</sub> [6], palladium dispersed on MgO [7,8], or supported on other metal oxides and zeolites [9,10] has been successfully tested in the Heck reaction for the arylation of styrene and acrylonitrile. However, the progressive deactivation as a result of

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the palladium leaching during the reaction could be a serious disadvantage for these supported catalysts. Instead, the anchoring of palladium complexes on polymers or inorganic substrates could assure a more lasting catalytic activity. High catalytic activities, selectivities and stabilities have been reported in the Heck reaction catalyzed by sulfur-containing polymeric palladium complexes [11,12], or by amino- and/or pyridine-functionalized silica-supported palladium catalysts [13–15]. Polymer-anchored palladium catalysts have also been used in the carbonylation of organic halides to oxo esters at mild pressure [16].

This paper mainly deals with the preparation and characterization of palladium complexes anchored on silica functionalized with chelating nitrogen ligands. These systems have been successfully tested as many times re-usable catalysts for the Heck reaction of iodobenzene with ethyl acrylate and styrene, and for the carbonylation of iodobenzene in methanol to methyl benzoate at atmospheric pressure.

## 2. Experimental

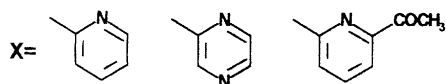
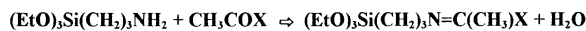
### 2.1. Catalyst preparation

The silica-anchored palladium catalysts were prepared by the following steps:

- synthesis of the Schiff-bases from 3-aminopropyltriethoxysilane (APS) and 2-acetylpyridine, 2-acetylpyrazine or 2,6-diacetylpyridine, respectively;
- reduction of the Schiff-bases with  $\text{NaBH}_4$  in methanol;
- cogelification with tetraethyl orthosilicate (TEOS);
- reaction of the functionalized silica with  $[\text{PdCl}_2(\text{PhCN})_2]$ .

#### 2.1.1. Synthesis of the Schiff-bases

Schiff-bases were prepared from APS by the following reaction:



(1)

Table 1

Reactions of the formation of the Schiff-bases

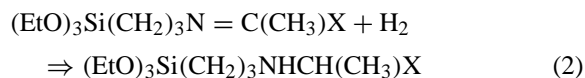
Carbonyl compound (CC)	CC (mmol)	APS (mmol)	Conversion, CC (%)
2-Acetylpyridine <sup>a</sup>	25.8	24.5	99
2,6-Diacetylpyridine <sup>a</sup>	10.0	20.0	91
2-Acetylpyrazine <sup>a</sup>	9.0	7.2	71
2-Acetylpyridine <sup>b</sup>	13.4	12.8	94
2,6-Diacetylpyridine <sup>b</sup>	4.9	10.1	100
2-Acetylpyrazine <sup>b</sup>	6.3	4.2	99

<sup>a</sup> Catalyst:  $\text{NH}_3$  aq. 0.2 N.<sup>b</sup> Catalyst:  $\text{NH}_4\text{F}$ .

The reaction (1) was performed under nitrogen in dry toluene (40 ml) over 3 Å molecular sieves at room temperature for up to 7 days. The amounts of the reagents are reported in Table 1. The conversion of  $\text{CH}_3\text{COX}$  was monitored by GC. After removal of the molecular sieves, the products were isolated by evaporation of toluene at reduced pressure. The formation of the Schiff-bases was confirmed by FTIR spectroscopy.

#### 2.1.2. Reduction of the Schiff-bases

The Schiff-bases were reduced to secondary amines by the following reaction:



A suspension of an excess of  $\text{NaBH}_4$  in methanol (30 ml) was quickly dropped in a flask containing the Schiff-base at 40 °C, then the mixture was heated in refluxing methanol until the development of hydrogen ceased.

#### 2.1.3. Formation of the functionalized silica gels

$(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHCH}(\text{CH}_3)\text{X}$  was mixed in a two-necked flask with tetraethoxysilane,  $\text{Si}(\text{OEt})_4$  (TEOS) in a 1:9 M ratio, then ethanol (25 ml) was added and an excess of 0.2 N ammonia solution was dropped into  $[\text{mmol H}_2\text{O} = 7(4x + 3y)]$ , where  $x = \text{mmol TEOS}$  and  $y = \text{mmol } (\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHCH}(\text{CH}_3)\text{X}$ . The amounts of reagents and catalyst used are reported in Table 2. The reaction mixture was stirred for 1 h, then allowed to stand for several hours until gelation. The gelified product was filtered on Buchner, then washed with water and ethanol, dried overnight at 60 °C in vacuo, finally crushed and sieved to >40 mesh.

Table 2

Preparation of the functionalized silica gels

Functionalized gel	Functionalized silane	Silane (mmol)	TEOS (mmol)	Catalyst (ml)
SILPY <sup>a</sup>	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> NHCH(CH <sub>3</sub> )py <sup>c</sup>	8.4	76.2	45
SILPZ <sup>a</sup>	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> NHCH(CH <sub>3</sub> )pz <sup>d</sup>	5.1	47.1	27
SILDIPY <sup>a</sup>	[(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> NHCH(CH <sub>3</sub> )] <sub>2</sub> py <sup>c</sup>	9.1	81.9	48
SILPY <sup>b</sup>	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> NHCH(CH <sub>3</sub> )py <sup>c</sup>	12.0	48.0	10
SILPZ <sup>b</sup>	(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> NHCH(CH <sub>3</sub> )pz <sup>d</sup>	4.2	38.2	10
SILDIPY <sup>b</sup>	[(EtO) <sub>3</sub> Si(CH <sub>2</sub> ) <sub>3</sub> NHCH(CH <sub>3</sub> )] <sub>2</sub> py <sup>c</sup>	4.9	43.9	10

<sup>a</sup> Catalyst: NH<sub>3</sub> aq. 0.2 N.<sup>b</sup> Catalyst: NH<sub>4</sub>F.<sup>c</sup> Pyridine radical.<sup>d</sup> Pyrazine radical.

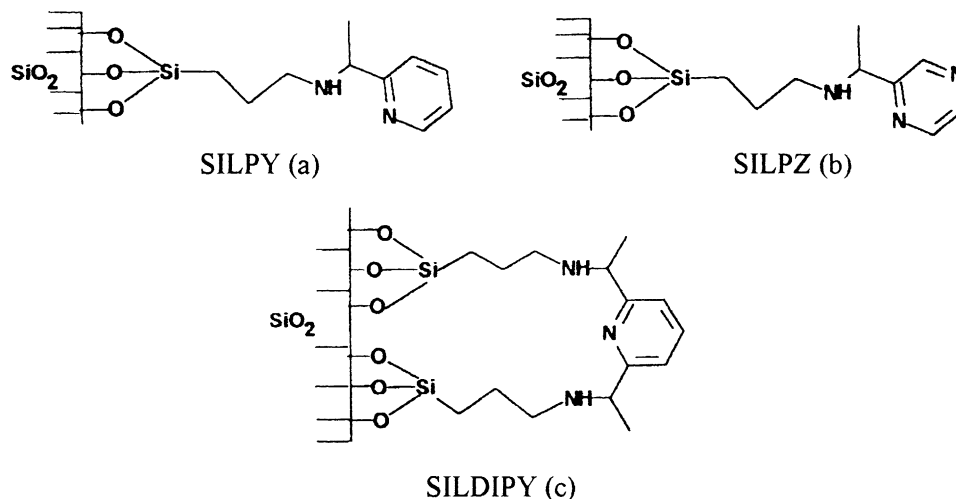
In another way of preparation, after mixing in a crystallizer (EtO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>NHCH(CH<sub>3</sub>)X with TEOS in the 1:9 M ratio, ethanol (30 ml) and an excess of water containing previously dissolved NH<sub>4</sub>F in a 1:100 M ratio to the sum (EtO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>NHCH(CH<sub>3</sub>)X + TEOS were added. Gelation occurred almost immediately. The obtained gel was allowed to stand for several days in air, then crushed up to >40 mesh, washed with water and ethanol, finally dried overnight at 60 °C in vacuo.

The three functionalized silica gels prepared from 2-acetylpyridine (SILPY) (a), 2-acetylpyrazine (SILPZ) (b) and 2,6-diacetylpyridine (SILDIPY) (c) have the following structures:

#### 2.1.4. Preparation of the anchored palladium complexes

[PdCl<sub>2</sub>(PhCN)<sub>2</sub>] was previously prepared, by dissolving PdCl<sub>2</sub> at 100 °C in a minimum amount of benzonitrile (15 ml PhCN/g PdCl<sub>2</sub>), then cooling and adding hexane to precipitate the complex. [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] was then isolated by filtering, washed twice with hexane and pentane, finally dried at 40 °C at moderately reduced pressure.

To prepare the anchored palladium complexes, [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the calculated amount of the functionalized silica was added. The suspension was maintained 4 h under stirring, then the only physisorbed complex was extracted in a Soxhlet apparatus with refluxing



$\text{CH}_2\text{Cl}_2$  for 3 h. The solid was finally dried overnight at  $50^\circ\text{C}$  in vacuo. The amount of anchored palladium was determined by the weight increase of the functionalized support.

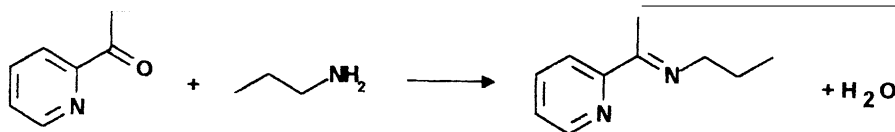
### 2.1.5. Reduction of palladium to Pd (0)

The functionalized silica-anchored Pd (II) was reduced to metal Pd (0) by a suspension of  $\text{NaBH}_4$  in methanol. The reduction was performed at  $40^\circ\text{C}$ , by dropping the reducing reagent into a flask containing an amount of the anchored complex corresponding to 0.015 g of palladium suspended in 10 ml of methanol. When the development of hydrogen has ceased, few milliliters of water were added to extinguish the reaction. The black reduced catalyst was then filtered, washed with water, methanol and  $\text{CH}_2\text{Cl}_2$ , finally dried under nitrogen at  $40^\circ\text{C}$  at reduced pressure.

## 2.2. Preparation of the model ligands and palladium complexes

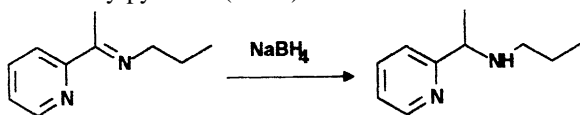
The model ligands and palladium complexes were prepared by the following reaction steps:

- (a) Preparation of the Schiff-bases from the reaction of *n*-propylamine with the pyridine or pyrazine compound, e.g. for 2-acetylpyridine:



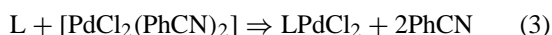
The reaction was performed under nitrogen with an excess of amine in dry toluene over 3 Å molecular sieves at room temperature for up to 7 days. The conversion of carbonyl compound was monitored by GC. After removal of the molecular sieves, the products were isolated by evaporation of unreacted amine and toluene at reduced pressure. The formation of the Schiff-bases was confirmed by FTIR spectroscopy.

- (b) Reduction of the Schiff-bases to secondary amines with  $\text{NaBH}_4$ , e.g. for the ligand with 2-acetylpyridine (LIPY):



The reduction was performed by dropping a suspension of  $\text{NaBH}_4$  in methanol into the flask containing the Schiff-base previously heated at  $40^\circ\text{C}$ . When the development of hydrogen has ceased the mixture was cooled to room temperature and water (30 ml) was added to extinguish the reaction. The amine ligands were recovered by adding few drops of  $\text{NaOH}$  0.1 N, then extracting with  $\text{CH}_2\text{Cl}_2$ . The organic extract, after evaporation of the solvent, was analyzed by FTIR, GC-MS and  $^1\text{H-NMR}$  spectra.

- (c) Reaction of the amine bidentate ligand, L, with  $[\text{PdCl}_2(\text{PhCN})_2]$ , under stirring, in a minimum amount of  $\text{CH}_2\text{Cl}_2$ . The exchange reaction (3):

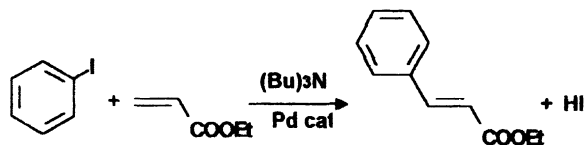


occurred almost immediately and gave rise to the precipitation of the palladium complex, which was recovered by filtering, washed with  $\text{CH}_2\text{Cl}_2$ , hexane and pentane, finally dried overnight at  $50^\circ\text{C}$  in vacuo. The model palladium complexes were characterized by FTIR,  $^1\text{H-NMR}$  and elemental C-H-N analysis.

## 2.3. Reaction tests

The catalytic activity of the prepared silica-anchored palladium complexes has been tested for:

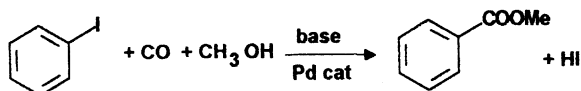
- (a) The Heck reaction from iodobenzene and ethyl acrylate to ethyl cinnamate, or styrene to stilbene, in toluene or *p*-xylene as solvent, with tributylamine as base, for 2 h at  $110^\circ\text{C}$ , e.g.:



An amount of catalyst corresponding to 0.015 g Pd was always used. At the end of the reaction the catalysts were separated from the reaction mixture by filtration at about  $30^\circ\text{C}$ , washed with the reaction

solvent and re-used. The filtered liquid was then cooled in an ice-bath to precipitate the ammonium salt  $(\text{Bu})_3\text{NHI}$ . After a second filtration the conversions of reagents and the selectivities to products were determined by GC analyses by adding isopropylbenzene as internal standard.

- (b) The carbonylation reaction at atmospheric pressure of iodobenzene by bubbling CO, in refluxing methanol for 8 h, with triethylamine or  $\text{CH}_3\text{COOK}$  as base, to methyl benzoate:



An amount of catalyst corresponding to 0.015 g Pd was always used. At the end of the reaction the catalysts were separated from the reaction mixture by filtration and re-used many times. The conversions of reagents and the selectivities to the product were determined by GC analyses, by adding isopropylbenzene as internal standard.

#### 2.4. Characterization of products

The specific surface area of the functionalized silica gels was determined with a Micromeritics 2200 analyzer, by the one-point modified BET method, from the nitrogen volume adsorbed at the liquid nitrogen temperature.

FTIR spectra were measured with a Nicolet 5PC spectrometer.  $^1\text{H-NMR}$  spectra were recorded with a Bruker AC 100 spectrometer by using  $\text{CDCl}_3$  as diluent for the liquid samples and deuterated DMSO as solvent for the solid ones.

GC–MS analyses of samples, diluted with an excess of  $\text{CH}_2\text{Cl}_2$ , were performed with an HP 5890

instrument, equipped with a SE-52 packed column, and interfaced with a MS quadrupole HP 5971 analyzer. The GC analyses of the reaction products were performed with a DANI 3400 instrument equipped with a thermal conductivity detector. As packed columns the following were used: 2 m 20% Apiezon L on Chromosorb W-DMCS 100/120 mesh, for the arylation of ethyl acrylate; 1 m 10% SE-30 on Chromosorb W-AW 80/100 mesh, for the arylation of styrene; 2 m 20% OV 101 on Chromosorb W-DMCS 60/80 mesh, for the carbonylation of iodobenzene. He (80 ml/min) as carrier gas was always used. Elemental C–H–N analyses were performed with a Carlo Erba EA 1108 analyzer, based on GC separation.

### 3. Results and discussion

#### 3.1. Preparation of the Schiff-bases and amine ligands

The conversions of the carbonyl compounds are given in Table 1. The condensation reactions with APS were almost complete. The formation of the Schiff-bases was demonstrated by the presence in the FTIR spectra of the absorption peak at about  $1640\text{ cm}^{-1}$ , due to the C=N imine double bond, and the reduced intensity of the C=O absorption peak at  $1700\text{ cm}^{-1}$ .

To prepare the model ligands an excess of *n*-propylamine in the preparation of the Schiff-bases was always used; therefore, the conversion of carbonyl compounds was complete. After reduction with  $\text{NaBH}_4$  in methanol, the model ligands were characterized by GC–MS analyses, FTIR and  $^1\text{H-NMR}$  spectra. The GC–MS analyses evidenced the absence of by-products.

Table 3  
Elemental analyses of the functionalized silica gels

Functionalized silica	C/N ratio <sup>a</sup>	Elemental analysis <sup>a</sup> (%)		
		C	N	H
SILPY	4.3 (4.3)	16.14 (15.90)	3.72 (3.71)	4.33 (4.28)
SILPZ	2.6 (2.8)	8.40 (14.30)	3.24 (5.49)	2.10 (2.79)
SILDIPY	4.4 (4.0)	11.41 (17.00)	2.58 (3.99)	2.56 (2.90)

<sup>a</sup> Theoretical values in brackets.

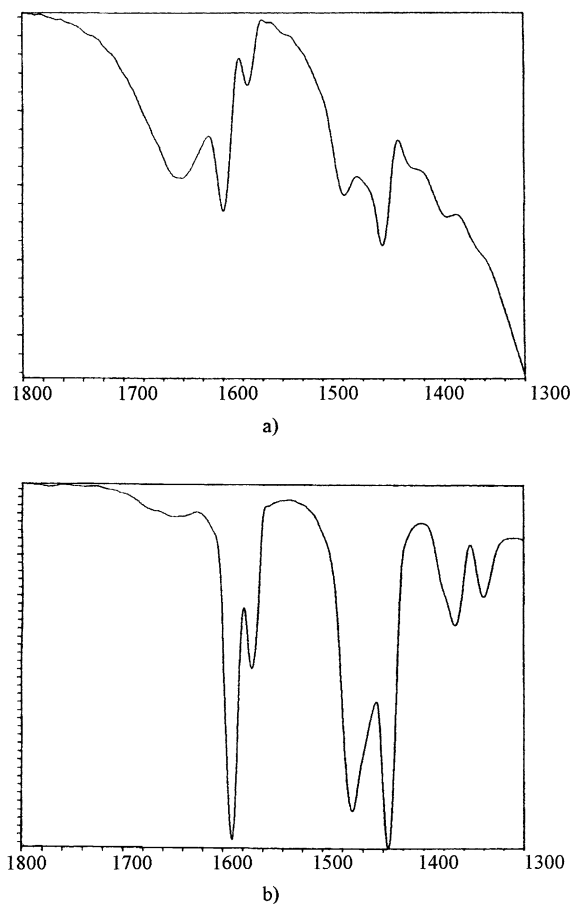


Fig. 1. FTIR spectra in the region  $1800\text{--}1300\text{ cm}^{-1}$ : (a) functionalized silica gel prepared from 2-acetylpyridine (SILPY: peaks at  $1599$ ,  $1574$ ,  $1485$  and  $1444\text{ cm}^{-1}$ ); (b) corresponding model ligand (LIPY: peaks at  $1590$ ,  $1571$ ,  $1471$  and  $1435\text{ cm}^{-1}$ ).

### 3.2. Preparation of the functionalized silica gels

The elemental analyses of the functionalized silica gels prepared with aqueous ammonia as catalyst (Table 3) were according to the theoretical values only in the case of the product from 2-acetylpyridine (SILPY). It is evident, for the other products, a C/N ratio near to the theoretical one, but in the presence of a silica excess, with a  $\text{SiO}_2/\text{SiO}_3/2(\text{CH}_2)_3\text{NHCHX}$  ratio higher than 9:1. There was a lower concentration of functionalizing groups in the recovered product because soluble oligomers probably formed in the hydrolysis and condensation steps, which remained in solution after washing and filtering the functionalized

Table 4

Surface area values and anchored palladium amounts on the functionalized silica gels

Functionalized silica	Surface area ( $\text{m}^2/\text{g}$ )	mmol Pd/g gel	Pd (%)
SILPY <sup>a</sup>	335.5	0.99	9.5
SILDIPY <sup>a</sup>	270.0	0.72	6.8
SILPZ <sup>a</sup>	365.4	0.50	4.9
SILPY <sup>b</sup>	18.0	0.79	7.4
SILDIPY <sup>b</sup>	75.4	0.65	6.2
SILPZ <sup>b</sup>	54.2	0.56	6.0

<sup>a</sup> Catalyst:  $\text{NH}_3$  aq. 0.2 N.

<sup>b</sup> Catalyst:  $\text{NH}_4\text{F}$ .

gels. Moreover, the formation of soluble oligomers in sol–gel processes is known from the literature [17].

In Fig. 1 a comparison is made between the FTIR spectra of the functionalized silica gel SILPY and the corresponding model ligand in the range  $1800\text{--}1300\text{ cm}^{-1}$ , where the absorption peaks of aromatic C–H and N–H bonds are present. Even though the intensity of peaks is weakened by the lower concentration of the functionalizing groups on silica, there are at least four absorption peaks in perfect agreement.

The surface area values of the functionalized silica gels are reported in Table 4. The use of ammonia instead of ammonium fluoride as gelification catalyst, then a slower progress of the gelification process, clearly produced higher surfaces.

### 3.3. Preparation of anchored palladium complexes

The anchored palladium amounts from the complexation reactions of the functionalized silica gels with  $[\text{PdCl}_2(\text{PhCN})_2]$  are reported in the last two columns of Table 4. The highest amounts were obtained with the functionalized silica gel SILPY. The formation of the complex is evidenced, both in the FTIR spectrum of the functionalized silica SILPY (Fig. 2a) and of the model ligand (Fig. 2b) from a  $20\text{ cm}^{-1}$  shift to lower wavenumbers of the  $1600\text{ cm}^{-1}$  peak.

### 3.4. Catalytic activity tests

The catalytic activity of all prepared anchored palladium complexes in the arylation reaction of ethyl acrylate was studied. The best proven catalyst was

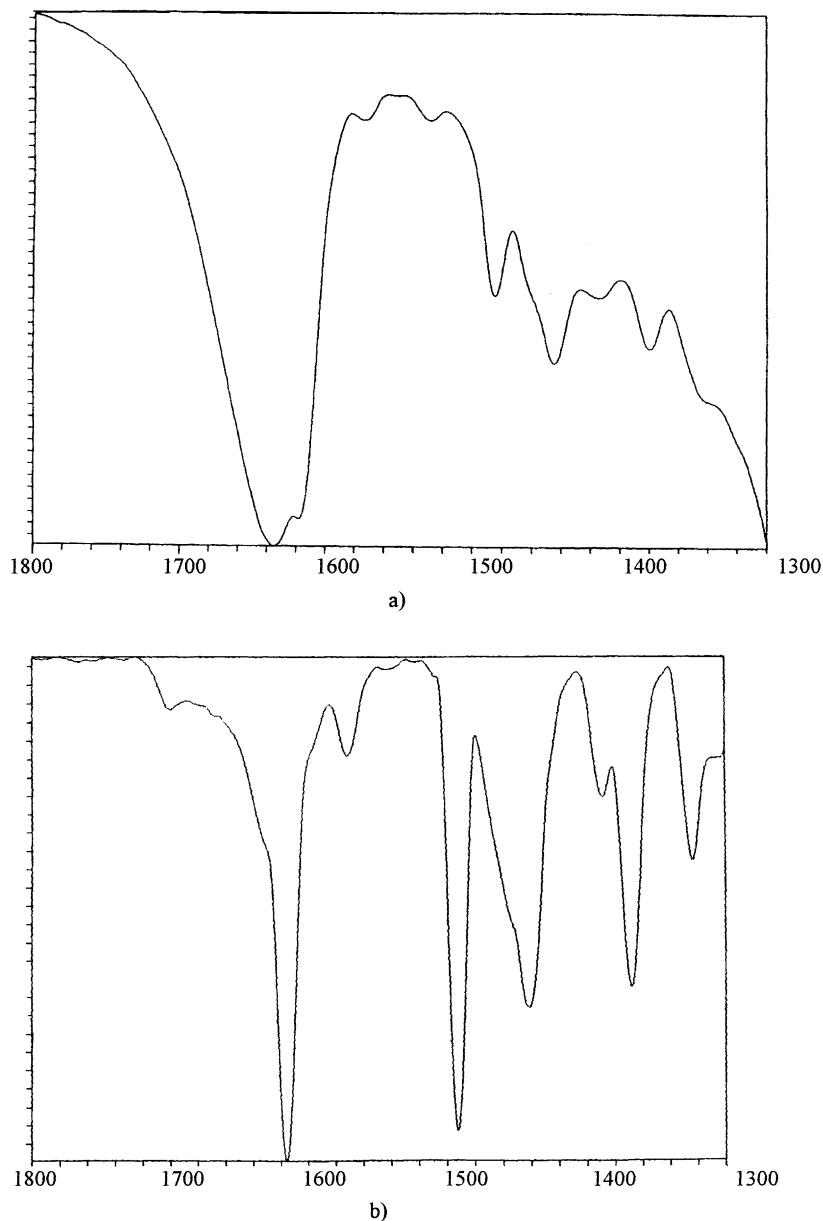


Fig. 2. FTIR spectra in the region 1800–1300  $\text{cm}^{-1}$  of the palladium complexes prepared from: (a) the functionalized silica gel prepared from 2-acetylpyridine (SILPY: peaks at 1618 and 1483  $\text{cm}^{-1}$ ); (b) the corresponding model ligand (LIPY: peaks at 1615 and 1492  $\text{cm}^{-1}$ ).

then tested for the arylation of styrene and the carbonylation of iodobenzene in methanol. A molar ratio of iodobenzene/palladium about 350:1, corresponding to about 0.2 g of anchored palladium complex, was always used.

#### 3.4.1. Heck reaction: arylation of ethyl acrylate

In a typical reaction test, iodobenzene (10.8 g = 51.6 mmol), ethyl acrylate (6.4 g = 64.2 mmol), tributylamine (10.1 g = 54.3 mmol), catalyst (0.2 g  $\approx$  0.015 g Pd  $\approx$  0.15 mmol Pd)

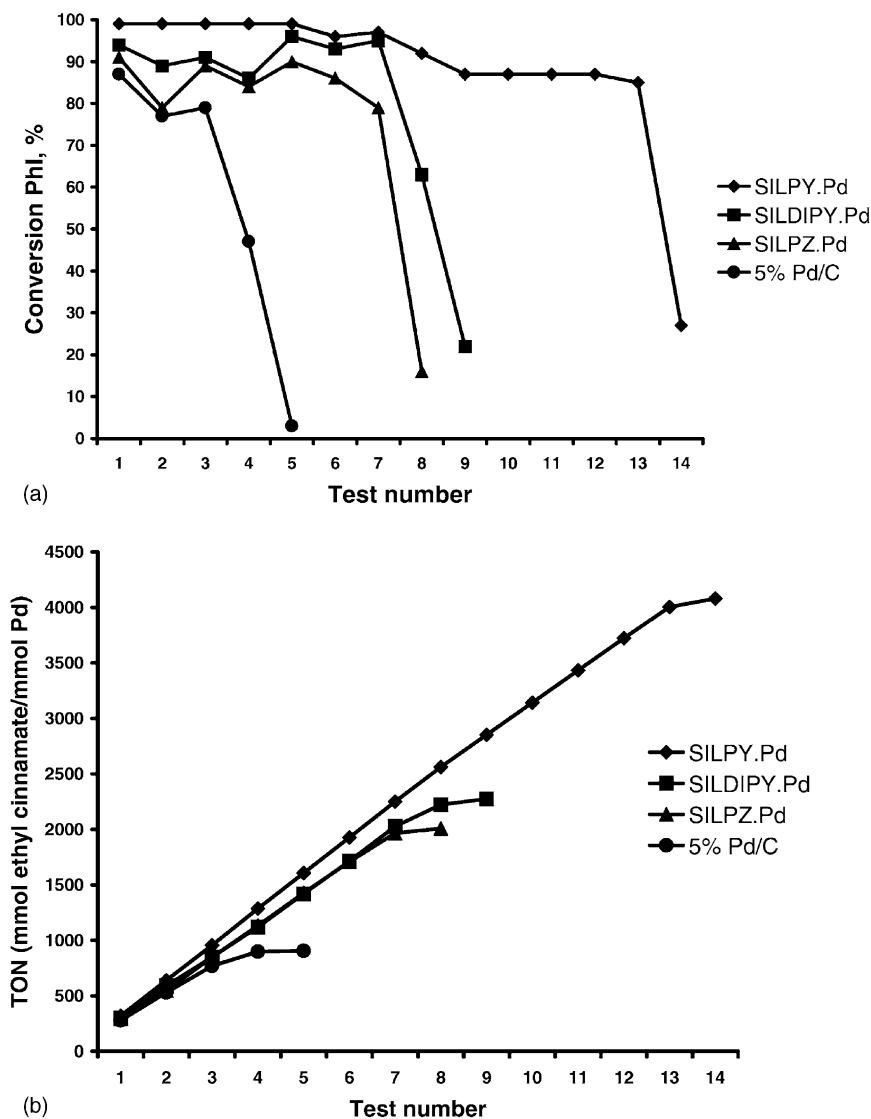


Fig. 3. Catalytic activity tests in the arylation of ethyl acrylate (toluene as solvent). Reaction time is 2h: (a) conversion of iodobenzene; (b) net production of ethyl cinnamate (TON, mmol product/mmol Pd).

and solvent (20 ml of toluene, or *p*-xylene) were used.

The results of the catalytic activity tests, both expressed as conversion of iodobenzene and net production of ethyl cinnamate (TON, mmol product/mmol Pd) are reported in Fig. 3 (toluene, as solvent) and Fig. 4 (*p*-xylene, as solvent), respectively. A commercial 5% Pd/C (Fluka) catalyst as comparison was tested.

Anchored palladium complexes were generally more active and more stable than the commercial Pd/C catalyst, probably due to the higher dispersion of the metal and the better resistance to leaching by the reaction solution. A better stability was observed in refluxing toluene as solvent, probably due to the lower reaction temperature, which also allowed a better control of temperature, then a less easy leaching.



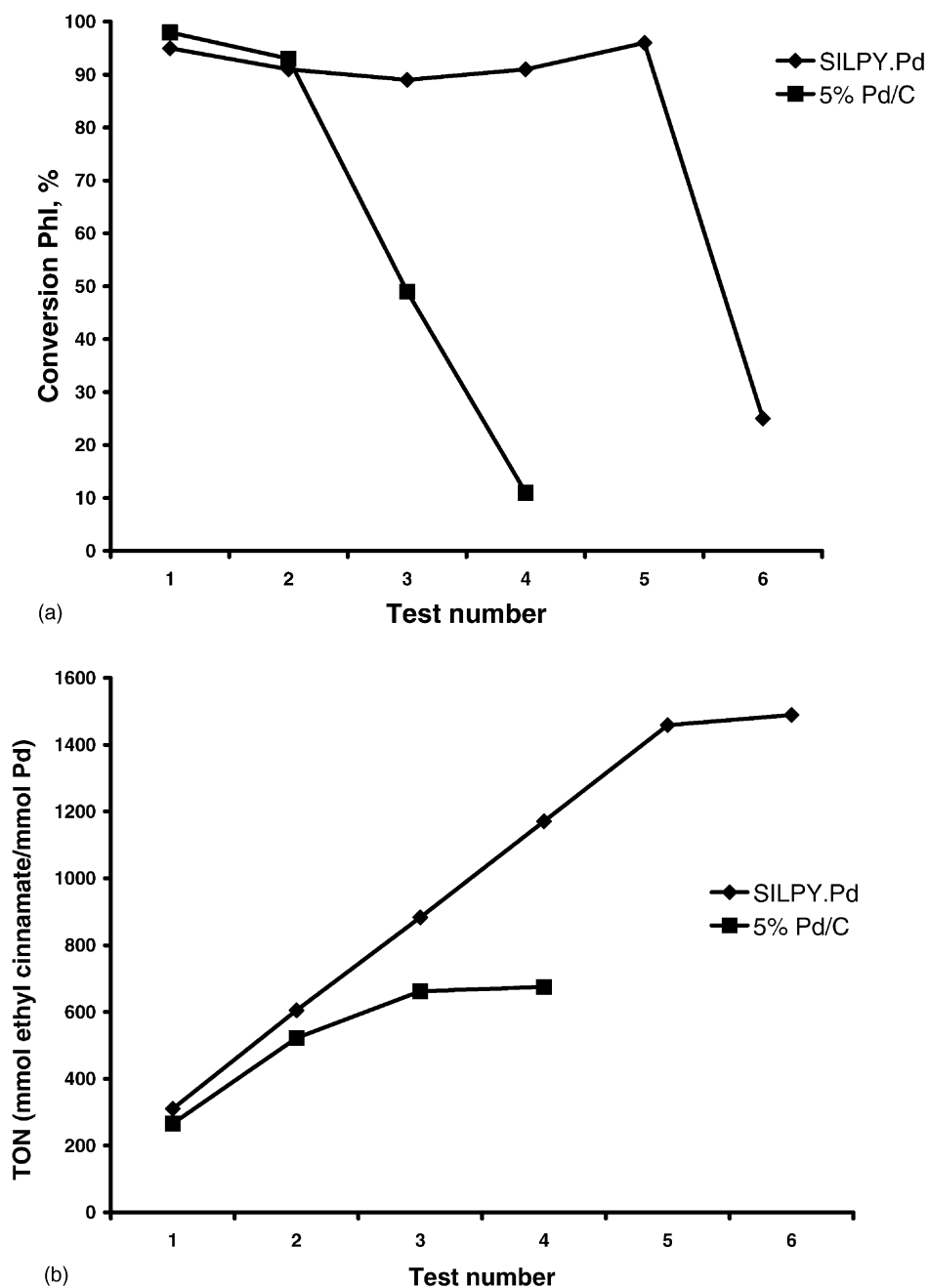


Fig. 4. Catalytic activity tests in the arylation of ethyl acrylate (*p*-xylene as solvent). Reaction time is 2 h: (a) conversion of iodobenzene; (b) net production of ethyl cinnamate (TON, mmol product/mmol Pd).

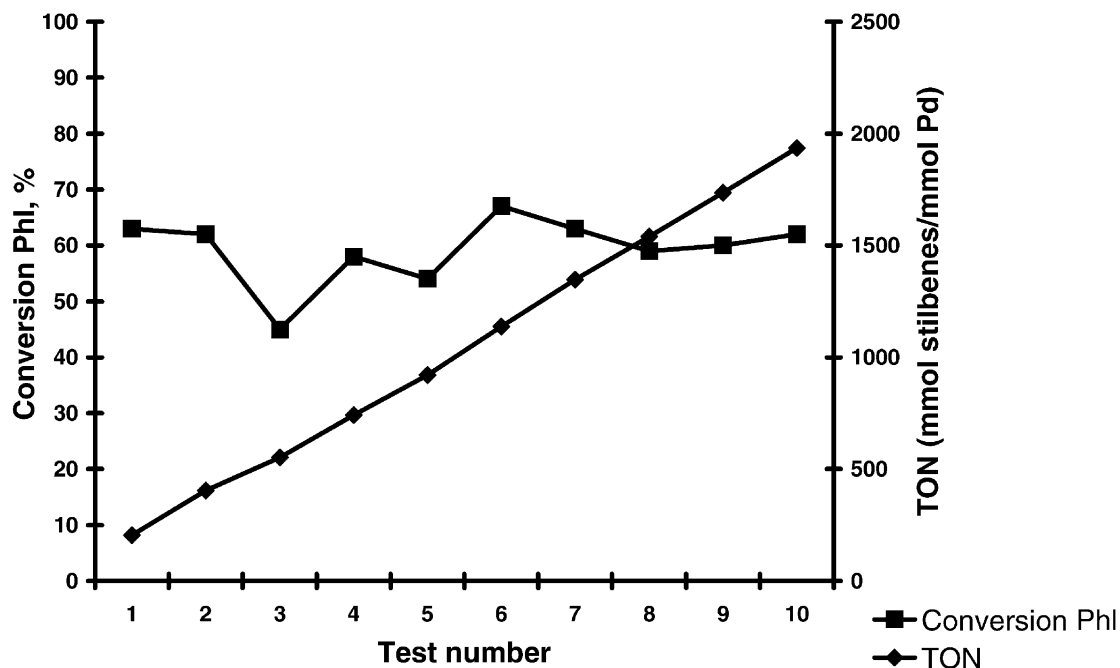


Fig. 5. Catalytic activity tests in the arylation of styrene: conversion of iodobenzene and net production of stilbenes (TON, mmol products/mmol Pd). Reaction time is 2 h, catalyst used is SILPY·Pd.

Fourteen reaction cycles before deactivation were performed with SILPY·Pd catalyst, prepared from SILPY·PdCl<sub>2</sub>, corresponding to a calculated TON (mmol ethyl cinnamate/mmol Pd) of about 4100. Therefore, SILPY·Pd catalyst was selected for testing in the arylation reaction of styrene to stilbene and in the carbonylation reaction of iodobenzene with methanol to methyl benzoate.

#### 3.4.2. Heck reaction: arylation of styrene

In a typical reaction test, iodobenzene (10.8 g = 51.6 mmol), styrene (6.4 g = 60.5 mmol), tributylamine (10.1 g = 54.3 mmol), catalyst (0.2 g SILPY Pd  $\approx$  0.015 g Pd  $\approx$  0.15 mmol Pd) and toluene (20 ml) as solvent were used.

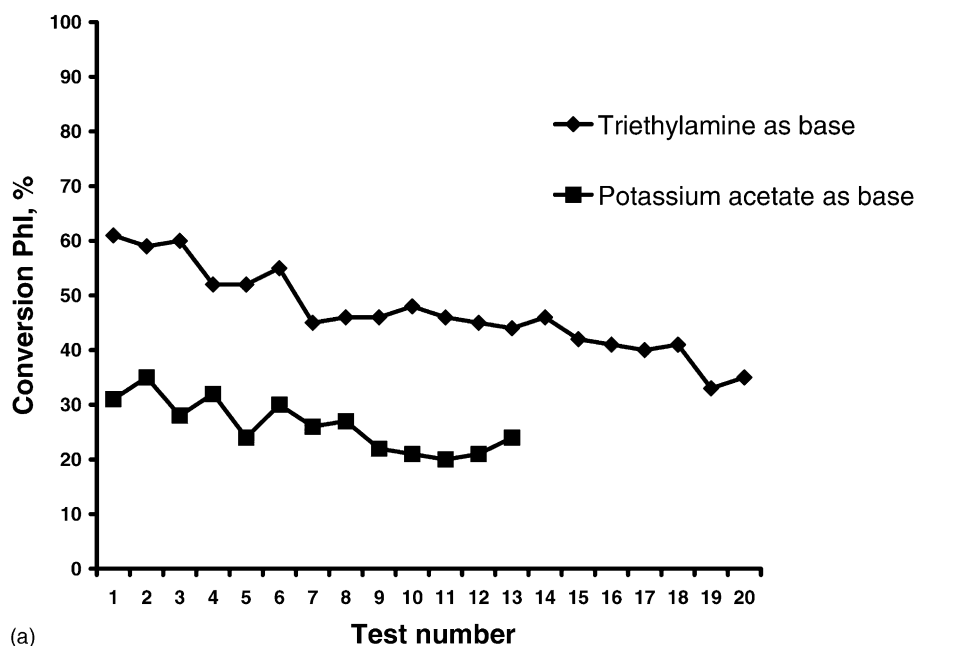
The results of the catalytic activity tests, both expressed as conversion of iodobenzene and net production of stilbenes (TON, mmol product/mmol Pd) are reported in Fig. 5. The catalytic activity practically kept constant during 10 reaction cycles and the selectivity to stilbenes was always much higher than 90%. The TON value (mmol stilbenes/mmol Pd) achieved about 2000 after the 10th test. The

*trans*-stilbene/*cis*-stilbene ratio was always higher than 8:1. The conversion of iodobenzene was lower than in the arylation of ethyl acrylate, due to the sterical hindrance of the styrene molecule, which slows down the reaction. A double length test (reaction time = 4 h) actually gave a very higher conversion (89%) of iodobenzene with a 97% selectivity to stilbenes.

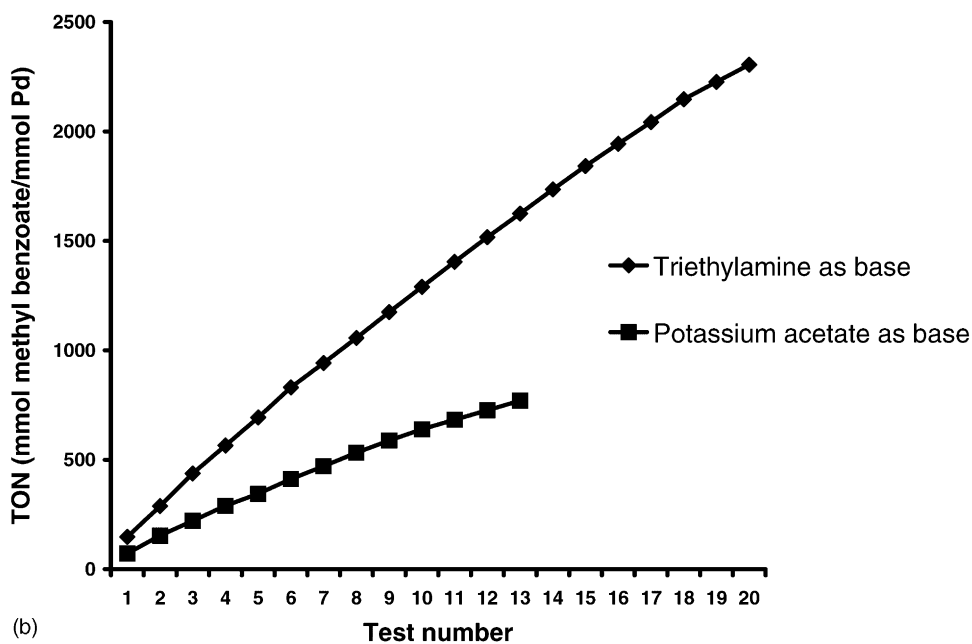
#### 3.4.3. Carbonylation of iodobenzene

In a typical reaction test, iodobenzene (8.2 g = 39.4 mmol), triethylamine (4.1 g = 40.9 mmol) or potassium acetate (4.6 g = 46.8 mmol) as base, catalyst (0.2 g SILPY · Pd  $\approx$  0.015 g Pd  $\approx$  0.15 mmol Pd) and methanol (30 ml) as reagent and solvent were used. The reaction tests were performed at 70 °C and atmospheric pressure under flowing CO for 8 h.

The results of the catalytic activity tests, both expressed as conversion of iodobenzene and net production of methyl benzoate (TON, mmol product/mmol Pd) are reported in Fig. 6. Using triethylamine, rather than potassium acetate, as base promoter, it was possible to perform 20 reaction cycles with a quite high



(a)



(b)

Fig. 6. Catalytic activity tests in the carbonylation of iodobenzene in methanol to methyl benzoate. Reaction time is 8 h, catalyst used is SILPY-Pd: (a) conversion of iodobenzene; (b) net production of methyl benzoate (TON, mmol product/mmolPd).

conversion of iodobenzene and a very high selectivity to methyl benzoate. The TON value (mmol methyl benzoate/mmol Pd) achieved about 2300 after the 20th test. A last test was performed with a higher reaction time (15 h): a 83% conversion of iodobenzene with a 97% selectivity to methyl benzoate was measured, so proving that the catalyst was still active.

#### 4. Conclusions

Palladium anchored on pyridine–amine functionalized silica exhibits high activity and selectivity in the arylation reactions of ethyl acrylate to ethyl cinnamate and styrene to stilbene, and in the carbonylation reaction of iodobenzene in methanol to methyl benzoate at atmospheric pressure. These heterogenized palladium catalysts are easily separable from the reaction mixture by filtering and are re-usable many times without deactivation by leaching of palladium.

Fourteen reaction cycles (TON = 4100 mmol ethyl cinnamate/mmol Pd) were performed in the Heck arylation of ethyl acrylate, while a commercial Pd/C catalyst deactivated after only three cycles. Good results with higher yields than reported in literature were obtained in the carbonylation of iodobenzene at atmospheric pressure, where 20 reaction cycles (TON = 2300 mmol methyl benzoate/mmol Pd) were performed without deactivation.

Therefore, the use of stable anchored palladium complexes can offer an interesting alternative to homogeneous catalysts for industrial applications.

#### Acknowledgements

This research was supported by MIUR (Cofin 1998 and Cofin 2000: “Metal clusters, basic and functional aspects”). The authors are grateful to Mr. P.A. Bonaldi for his technical assistance to GC analyses.

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