Heterogeneously catalysed Heck reaction using palladium modified zeolites

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Abstract

Palladium modified zeolites exhibit a high activity towards the Heck reaction of aryl bromides with styrene for small Pd concentrations (= 0.2 mol%). The catalysts can be easily separated from the reaction mixture and reused without loss in activity. Leaching of active Pd species was observed in dependence on the zeolite structure. The electronic nature of the aryl bromide has a dominating effect on the reaction yield and the results observed are consistent with an oxidative addition of the aryl bromide to a Pd(0) centre via a $S_N Ar$ route. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Heck reaction; Palladium modified zeolite; Aryl bromide

1. Introduction

The 1971 discovered Heck reaction, a palladium catalysed carbon–carbon bond formation between aryl halides and olefins, became an excellent tool for the synthesis of elaborated styrene derivatives due to its tolerance of a wide variety of functional groups on both partners [1,2].

While the use of soluble palladium complexes to promote this reaction is well established (high reactivity and high selectivity) [1–5], homogeneous catalysis is generally connected with the problem of separation (purity of the products), recovery and regeneration of the catalysts. In small scale synthesis these problems are solved by purification using chromatography accompanied by the loss of the catalysts, but for synthesis of industrial interest the costs of the catalyst materials are of importance. In addition to the separation problems, deactivation of the homogeneous catalysts by formation of inactive colloidal species are encountered at the comparatively high reaction temperature [6].

The problems discussed could be principally minimised by a heterogeneously catalysed Heck reaction [7,8]. However, only sporadic reports have appeared in the last 15 years for the activation of iodo- and bromo-benzenes in solution by Pd/C, Pd/MgO, Pd/Al$_2$O$_3$, Pd/SiO$_2$ [9–13], or more recently by immobilised palladium particles in MCM-41 [14]. Generally no data have been associated concerning the problem of dissolution of active species (leaching). Activation of chlorobenzenes has been reported, but only

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under drastic reaction conditions (high temperature, no solvent or reacting solvent such as MeOH) [14–16].

Although there is—to our knowledge—no report for the Heck reaction with zeolites, their use as support for Pd particles could have some advantages to overcome the problems of leaching using heterogeneous catalysts in solution [17,18]. In addition, zeolites are capable of stabilising small metal particles immobilised in their cavities and are widely used due to their well established shape-selectivity [19].

Here we report for the first time that palladium loaded zeolites are highly active, selective and recoverable heterogeneous catalysts towards the Heck reaction of aryl bromides with styrene. The phenomenon of leaching, particularly the relation between leaching and zeolite structure, have been studied in detail.

2. Experimental

All preparations, manipulations and reactions were carried out under argon, including the transfer of the catalyst to the reaction vessel. All glassware was base- and acid-washed and oven dried. The chemicals (organic reagents and solvent) were deaerated by an argon flow before they were used. NMR spectra were recorded with a Bruker AM 400 spectrometer (^{1}H NMR were referenced to the residual protio-solvent: $CDCl_3$, $\delta = 7.25$ ppm; ^{13}C NMR were referenced to the C-signal of the deutero solvent: $CDCl_3$, $\delta = 77$ ppm). The palladium content determination of the exchanged zeolites was performed by AAS.

2.1. Catalyst preparation

The palladium loaded catalysts were prepared, according to the literature [20,21] by ion exchange, using a 0.1 M aqueous solution of $[Pd(NH_3)_4]^{2+}$, $2Cl^-$. Calcination at 500°C under pure O_2 (180 ml/min) of the exchanged $[Pd(NH_3)_4]^{2+}$ zeolites gave immobilised Pd(II)

species in sodalite cages (or adjacent cages), and subsequent treatment at 350°C with pure H_2 (70 ml/min) gave immobilised Pd(0) species in zeolite super-cages (Scheme 1).

2.1.1. General procedure for the preparation of the palladium modified zeolites

A 0.1 M ammoniac solution of $[Pd(NH_3)_4]Cl_2$ (prepared from $PdCl_2$ and a commercial ammoniac solution) was added drop-wise to a suspension of the zeolite (H- or Na-Mordenite, H-Y) in bidistilled water (100 ml/g zeolite). The mixture was stirred for 24 h at r.t. and the exchanged zeolite was filtered off and washed until no trace of chloride was detected in the filtrate ($AgNO_3$ test). Then the zeolite was allowed to dry at room temperature to give the entrapped $[Pd(NH_3)_4]^{2+}$ zeolite as a slightly yellow material.

The Pd(II) exchanged zeolite was obtained by calcination of the entrapped $[Pd(NH_3)_4]^{2+}$ zeolite in a U-reactor under a pure oxygen flow (180 ml/min) using a heating rate of 2 K/min from r.t. to 500°C. The temperature was maintained at 500°C for 30 min and the reactor was cooled to room temperature under a flow of argon to give the modified Pd(II) zeolite as a tabac-colored powder. (Note: The Y zeolites with a SiO_2/Al_2O_3 ratio of 4.7 gave a pink zeolite.) The Pd(II) loaded zeolites were then stored under an Ar atmosphere to prevent hydration.

The Pd(0) exchanged zeolite was obtained by reduction of the Pd(II) zeolite in a U-reactor under a pure hydrogen flow (70 ml/min) using a heating rate of 8 K/min from r.t. to 350°C. The temperature was maintained at 350°C for 15 min and the reactor was cooled to room
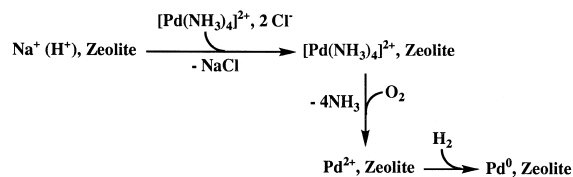
Scheme 1.

temperature under a flow of argon to give the Pd(0) modified zeolite as a black powder. The Pd(0) loaded zeolites were then stored under an Ar atmosphere to prevent re-oxidation.

The absolute palladium content was determined by AAS spectroscopy for the supernatant solution and for the zeolites after ion exchange, calcination and reduction from a solution obtained by treatment with a mixture of HBF_4, HNO_3 and HCl in a Teflon reactor at $180°C$. The AAS gave for the lowest loaded zeolite $4 \pm 0.5\%wt$ Pd (for a 5%wt ion-exchange experiment, quoted in the text as 4% zeolite) and for the highest $7 \pm 0.5\%wt$ Pd (for a 10%wt ion exchange experiment, quoted in the text as 7% zeolite).

2.2. Test of the catalytic activity

The catalytic reactions were carried out in pressure tubes under argon. The qualitative and quantitative analysis of the reactants and the products was made by gas liquid chromatography. Conversion and selectivity are represented by product distribution (= relative area of GLC-signals), and GLC yields in parentheses (= relative area of GLC-signals referred to an internal standard calibrated to the corresponding pure compound, $\Delta_{rel} = \pm 10\%$). Where available, yields in isolated products are given in brackets. In the text and tables, Pd(II) refers to Pd species immobilised in zeolite by ion-exchange subsequently treated by calcination under O_2 flow and Pd(0) refers to Pd species immobilised in zeolite by ion-exchange subsequently treated by calcination under O_2 flow followed by reduction with H_2. The catalysts were transferred under Ar.

2.2.1. General procedure for the first run and the recycling of the catalysts

10 mmol of aryl halide, 15 mmol of styrene, 15 mmol of NaOAc and 0.2 mol% of Pd (as heterogeneous catalysts, the amount in g of catalysts depending of the palladium concentration) were introduced in a pressure tube under argon. 8 ml of solvent (DMAc p.a. previously deaerated) were added and the mixture was deaerated by an argon flow for 5 min. The reactor was then placed in a pre-heated oil bath at $140°C$ for 20 h with vigorous stirring and then cooled to room temperature before the reaction mixture was analysed by GLC.

For the recycling studies, a catalyst issue from a first run was used. After separation of the reaction mixture, it was washed with toluene and CH_2Cl_2 in order to remove adsorbed organic substrates and dried at room temperature.

2.2.2. General procedure for the examination of the presence of catalytically active species in homogeneous / bulk solution ('leaching')

A clear filtrate of the first run of the catalyst (obtained by filtration using a microglass Whatman filter in order to remove the fine particles) was used as solvent basis for these experiments. The filtrate (free of catalyst) was placed in a pressure tube and deaerated by an Ar flow for 5 min. Then, new organic reactants were added under argon atmosphere: 10 mmol of aryl halide, 15 mmol of styrene, 15 mmol of NaOAc and well homogenised. A GLC analysis of the composition of the mixture was made before the reactor was placed in a pre-heated oil bath at $140°C$ for 20 h with vigorous stirring. After the reaction, the reactor was cooled to room temperature and a second GLC analysis was performed. The comparison between the two GLC analyses gave a qualitative measure for the presence of active species in homogeneous/bulk solution.

2.2.3. GLC analysis

A homogeneous 3 ml sample of the reaction mixture was sampled and quenched with 3 ml of water in a test tube. The mixture was extracted with 2 ml of CH_2Cl_2 and the organic layer was filtered through a $MgSO_4$ pad. The resulting dry organic layer was then analysed by GLC. GLC-rate program: AS 100: 2 min at $100°C$, heating 15 K/min up to $170°C$, 2 min at $170°C$, heating 35 K/min up to $240°C$, 10 min

at 240°C, heating 50 K/min up to 270°C and 2 min at 270°C.

2.2.4. Purification of the trans-stilbene products 3

After the separation of the heterogeneous catalyst, the reaction phase was added to CH_2Cl_2 (50 ml) and washed with H_2O (3 × 15 ml). The organic layer was separated and dried over $MgSO_4$ and evaporated. The residue was dissolved in 15 ml of CH_2Cl_2 and added to pentane (8 ml). The solution was placed at −18°C to give the *trans*-stilbene **3** which was collected by filtration. The mother liquor was concentrated, treated as the original liquor to give additional product. The purity of the product was estimated by GLC to be ≥ 99.8%.

Data for R = F: ^{1}H NMR, CDCl$_3$, 400.13 MHz: 7.35–7.40 (m, 4H, *ortho*-vinyl-C_6H_4F and *ortho*-vinyl-C_6H_5); 7.26 (pseudo-t, 2H, *meta*-vinyl-C_6H_5); 7.16 (m, 1H, *para*-vinyl-C_6H_5); 6.92–6.96 (m, 4H, *ortho*-F–C_6H_4F and C*H*-vinyl).

^{13}C NMR, CDCl$_3$, 400.13 MHz: 161.06 (C–F–C_6H_4F); 137.13 (C-vinyl-C_6H_5); 133.50 (C-vinyl-C_6H_4F); 128.67 (*meta*-vinyl-C_6H_5); 128.45 and 128.46 (*ortho*-vinyl-C_6H_4F); 127.99 and 127.92 (C*H*-vinylic); 127.44 (*para*-vinyl-C_6H_5); 126.42 (*ortho*-vinyl-C_6H_5); 115.68 and 115.47 (*meta*-vinyl-C_6H_4F).

Data for R = NO$_2$: ^{1}H NMR, CDCl$_3$, 400.13 MHz: 8.15 (d, ^3J = 9.0 Hz, 2H, *ortho*-NO$_2$–C_6H_4NO$_2$); 7.57 (d, ^3J = 9.0 Hz, 2H, *ortho*-vinyl-C_6H_4NO$_2$); 7.50 (d, ^3J = 7.5 Hz, 2H, *ortho*-vinyl-C$_6H_5$); 7.35 (pseudo-t, ^3J = 7.0 Hz, 2H, *meta*-vinyl-C$_6H_5$); 7.16 (pseudo-q, ^3J = 7.0 Hz, 1H, *para*-vinyl-C$_6H_5$); 7.21 (d, ^3J = 16.6 Hz, 1H, C*H*-vinyl); 7.08 (d, ^3J = 16.6 Hz, 1H, C*H*-vinyl).

^{13}C NMR, CDCl$_3$, 400.13 MHz: 146.47 (C–NO$_2$–C_6H_4NO$_2$); 143.64 (C-vinyl-C_6H_4NO$_2$); 135.93 (C-vinyl-C_6H_5); 133.07 (*meta*-vinyl-C_6H_5); 128.65 (*ortho*-vinyl-C_6H_4NO$_2$); 128.60 (*para*-vinyl-C_6H_5); 126.80 and 126.64 (C*H*-vinylic); 126.00 (*ortho*-vinyl-C_6H_5); 123.85 (*meta*-vinyl-C_6H_4NO$_2$).

Data for R = CH$_3$CO: ^{1}H NMR, CDCl$_3$, 400.13 MHz: 7.82 (d, ^3J = 8.3 Hz, 2H, *ortho*-CH$_3$CO–C_6H_4CH$_3$CO); 7.45 (d, ^3J = 8.0 Hz, 2H, *ortho*-vinyl-C_6H_4CH$_3$CO); 7.41 (d, ^3J = 7.0 Hz, 2H, *ortho*-vinyl-C_6H_5); 7.26 (pseudo-t, ^3J = 7.3 Hz, 2H, *meta*-vinyl-C_6H_5); 7.18 (pseudo-q, ^3J = 7.0 Hz, 1H, *para*-vinyl-C_6H_5); 7.10 (d, ^3J = 16.6 Hz, 1H, C*H*-vinyl); 7.00 (d, ^3J = 16.6 Hz, 1H, C*H*-vinyl); 2.47 (s, 3H, C*H$_3$*CO).

^{13}C NMR, CDCl$_3$, 400.13 MHz: 197.05 (CH$_3$*C*O); 141.56 (C-vinyl-C_6H_4CH$_3$CO); 136.22 (C–CH$_3$CO–C_6H_4CH$_3$CO); 135.45 (C-vinyl-C_6H_5); 130.99 (*meta*-vinyl-C_6H_5); 128.43 (*meta*-vinyl-C_6H_4CH$_3$CO); 128.36 (*ortho*-vinyl-C_6H_4CH$_3$CO); 127.83 (*para*-vinyl-C_6H_5); 126.95 (*ortho*-vinyl-C_6H_5); 126.40 and 126.08 (C*H*-vinylic); 26.11 (C*H$_3$*CO).

Data for R = H: ^{1}H NMR, CDCl$_3$, 400.13 MHz: 7.64 (d, ^3J = 7.0 Hz, 4H, *ortho*-vinyl-C$_6H_5$); 7.48 (pseudo-t, ^3J = 7.5 Hz, 4H, *meta*-vinyl-C_6H_5); 7.39 (pseudo-t, ^3J = 7.0 Hz, 2H, *para*-vinyl-C_6H_5).

^{13}C NMR, CDCl$_3$, 400.13 MHz: 137.28 (C-vinyl-C_6H_5); 128.63 (*meta*-vinyl-C_6H_5); 128.48 (C*H*-vinylic); 127.56 (*para*-vinyl-C_6H_5); 126.48 (*ortho*-vinyl-C_6H_5).

3. Results and discussion

In a first step it was investigated how the catalytic properties of the palladium modified zeolites are influenced by:
1. the palladium loading
2. the zeolite structure (Mordenite- or Y-type)
3. the zeolite counter-ion (H- or Na-form) and
4. the palladium oxidation state [Pd(II) or Pd (0)].

We choose the reaction of styrene with bromofluorobenzene as model reaction (Scheme 2). This reaction is known to give high yields of Heck product with homogeneous catalysts, thereby allowing the observation of small changes in activity and selectivity.
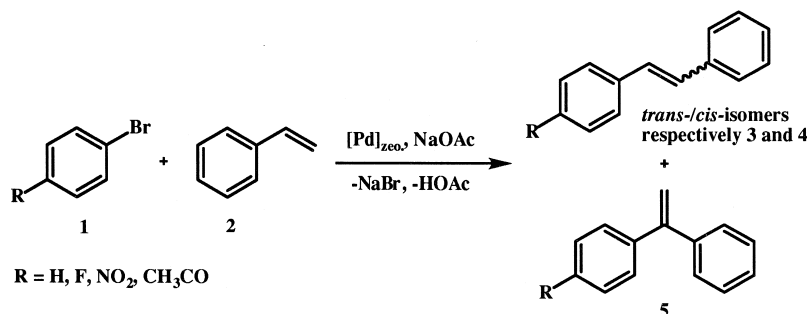
Scheme 2. Reaction conditions: 10 mmol bromofluorobenzene, 15 mmol styrene, 15 mmol NaOAc, 0.2 mol% $[Pd]_{zeo}$., 8 ml DMAc, 140°C, 20 h.

3.1. Influence of the palladium loading

As reported in the literature, the particle size of immobilised palladium is influenced by the temperature of the reduction rather than the absolute palladium quantity (%Pd) [22–26]. The conversion and the selectivity obtained for the two rather similarly loaded Pd(0) zeolites (4% and 7%) do not show an influence due to the palladium loading for an identical absolute amount of Pd (0.2 mol%) used in the Heck reaction. Namely, a yield for the *trans*-stilbene product **3** of 85% was obtained (corresponding to a conversion of > 95% of the aromatic educt **1**) with a product selectivity **3:4:5** equal to 85:1:9 for both loading.

3.2. Influence of the zeolite structures and the zeolite counter-ion (H- or Na-)

The goal of the following experiments was to investigate the catalytic activity in dependence on the zeolite nature in order to: (1) obtain the highest activity for the catalysts, (2) minimise the leaching, (3) obtain stable reusable catalysts. Two zeolites with a different structure, the Mordenite and the Y were used for these experiments [27].

The conversion and the selectivity obtained for 7% Pd(0) loaded Mordenite and Y zeolites are listed in Table 1.

The results do not show a dependence concerning the reaction yields or the product selectivity (a product shape-selectivity could be ex-pected with the Mordenite due to the restricted window) on the heterogeneously catalysed Heck reaction as a function of the zeolite nature. Generally the Y zeolites gave slightly better yields, probably due to the larger aperture of the supercage window. Concerning the zeolite structure (Mordenite or Y), a correlation with leaching was observed, which will be discussed later in this paper. Concerning the nature of the counter-ion (Na- or H-), kinetic experiments showed an unexpected dependence (discussed below) but no effect provided by the negatively charged zeolites framework (Na-form) was observed [28]. The Heck reaction being dependent on the presence of a base to regenerate the catalyst by abstraction of HBr, the Na-form was expected to favour the reaction by the presence $-O^- Na^+$ in the zeolite cages. Finally, an influence of the SiO_2/Al_2O_3 ratio was expected, since the zeolites with a SiO_2/Al_2O_3 ratio higher than 7 can be classified in the same family of generally acidic, but only a strong correlation with leaching was observed.

Table 1

Results obtained for the Heck reaction (Scheme 2) with 7% Pd(0) Mordenites (Na- or H-form) or H-Y zeolites

Entry	Zeolite type	**3** [%]	**4** [%]	**5** [%]
1	Na-Mordenite	84.9 (80.7)	0.9 (0.9)	7.9 (7.8)
2	H-Mordenite	85.1 (81.5)	1.0 (1.0)	7.8 (7.9)
3	H-Y, $SiO_2/Al_2O_3 = 4.7$	88.0 (86.7)	0.9 (1.0)	8.2 (8.4)
4	H-Y, $SiO_2/Al_2O_3 = 12$	89.4 (89.6)	0.9 (1.0)	8.2 (8.6)
5	H-Y, $SiO_2/Al_2O_3 = 25$	89.3 (89.3)	0.9 (1.0)	8.1 (8.5)

Product distribution and (GLC-Yields) are given ($\Delta_{rel} = \pm 10\%$).

3.3. Influence of the oxidation state of palladium

Different zeolites were modified with 7% Pd(0) or Pd(II) species. The results obtained from the catalytic experiments for the Heck reaction are listed in Table 2.

The results did not show a strong influence of the palladium oxidation state onto the product yields or the product selectivity. Generally the modified zeolites with Pd(II) species gave slightly better results, particularly for the Mordenite based catalysts. To rationalise these observations, kinetic experiments were performed.

For Pd(II) modified H-Mordenite (Fig. 1a) an induction period of ca. 4 min is required before the reaction starts slowly. This starting period is not observed for the Pd(0) modified H-Mordenite, and already after a period of 30 s the products of the reaction could be detected. The curves obtained with the Pd(II) modified H-Mordenite are similar to the ones observed for homogeneous catalysis. The induction period corresponds to the delay required for the reduction of the catalyst precursor Pd(II) species to the active Pd(0). This reduction is probably caused both by the styrene [29], and by the OH groups present in the zeolite cages [30,31]. An indication of reduction of the Pd(II) species by OH-groups was indicated by kinetic experiments with a 7% Pd(II) modified Na-Mordenite. The induction period passed from 4 min for the H-form to 8 min for the Na-form and after this
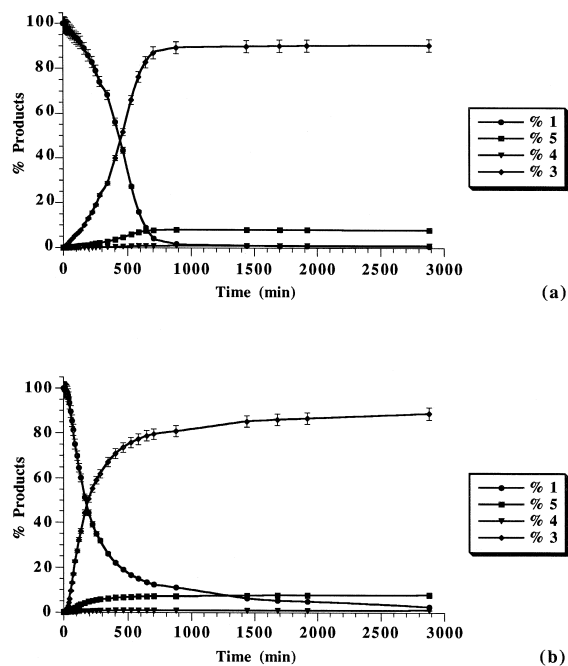

Fig. 1. Kinetic investigations: Conversion of educt **1** and products percentage (**3**, **4** and **5**) obtained with 7% Pd(II) H-Mordenite (a) and 7% Pd(0) H-Mordenite (b) for the Heck reaction (Scheme 2).

period the reaction proceeds as observed for the H-Mordenite. Using Pd(II) modified Na-Mordenite, a total transformation of the aryl halide is obtained after a reaction time of ca. 1900 min vs. 1450 min for the Pd(II) modified H-Mordenite.

These kinetic experiments showed that the heterogeneously catalysed Heck reaction proceeds faster using Pd(II) modified zeolites than the corresponding Pd(0) catalysts. As can be

Table 2

Results obtained for the Heck reaction (Scheme 2) with 7% Pd(0) or Pd(II) Mordenites (Na- or H-form) or H-Y zeolites

Entry	Zeolite type	Pd	**3** [%]	**4** [%]	**5** [%]
1	Na-Mordenite	Pd(0)	84.9 (80.7)	0.9 (0.9)	7.9 (7.8)
2	Na-Mordenite	Pd(II)	89.6 (92.0)	1.0 (1.0)	8.3 (8.9)
3	H-Mordenite	Pd(0)	85.1 (81.5)	1.0 (1.0)	7.8 (7.9)
4	H-Mordenite	Pd(II)	89.7 (90.8)	0.9 (1.0)	8.4 (8.9)
5	H-Y, $SiO_2/Al_2O_3 = 4.7$	Pd(0)	88.0 (86.7)	0.9 (1.0)	8.2 (8.4)
6	H-Y, $SiO_2/Al_2O_3 = 4.7$	Pd(II)	90.1 (92.0)	1.0 (1.0)	8.3 (8.9)
7	H-Y, $SiO_2/Al_2O_3 = 12$	Pd(0)	89.4 (89.6)	0.9 (1.0)	8.2 (8.6)
8	H-Y, $SiO_2/Al_2O_3 = 12$	Pd(II)	90.2 (93.0)	1.0 (1.0)	8.4 (9.1)
9	H-Y, $SiO_2/Al_2O_3 = 25$	Pd(0)	89.3 (89.3)	0.9 (1.0)	8.1 (8.5)
10	H-Y, $SiO_2/Al_2O_3 = 25$	Pd(II)	89.8 (91.5)	1.0 (1.0)	8.4.(8.9)

Product distribution and (GLC-Yields) are given ($\Delta_{rel} = \pm 10\%$).

deduced from Fig. 1 a reaction time of ca. 1450 min for the total transformation of the aryl halide with the Pd(II) modified zeolites is required, vs. ca. 7200 min with the Pd(0) modified zeolites. This result can be rationalised by the different treatment of the two catalysts during the reduction period. The in situ reduced Pd(II) catalyst leads to higher dispersed Pd(0) species in sodalite cages [22], since it is obtained by relatively low temperature treatment (140°C). In contrary, the reduced Pd(0) catalyst obtained by treatment under H_2 atmosphere at 350°C leads to palladium particles of ca. 20–30 Å in zeolite super cages [22]. These results suggest that there is a relation between the dispersion of the Pd(0) species in the zeolite and the activity of the catalysts.

3.4. Examination of the presence of catalytically active species in homogeneous bulk solution ('leaching')

The leaching of active species from heterogeneous catalysts in solution is a crucial question in order to identify whether the active centres are solid surfaces or dissolved palladium complexes. We have studied this phenomenon in more details.

The leaching was studied as followed: the organic phase of a first run was separated from the solid (Pd modified zeolite). New reagents

(p-BrFC$_6$H$_4$ **1**, styrene **2** and NaOAc) were added to the clear filtrate, and the composition of the reaction mixture was determined by GLC, the amount of p-BrFC$_6$H$_4$ **1** being set to 100%. This homogeneous reaction mixture was treated as a standard catalytic experiment (140°C, 20 h). After 20 h reaction time, the composition was determined by GLC again. The differences observed between the two GLC determinations give qualitative information about the 'leaching' phenomenon.

While this method does not allow the absolute quantification of the palladium species (active and/or inactive) dissolved by the leaching phenomenon, it gave information concerning the presence or absence of *active* species in bulk solution and an idea of the relative influence of these species on the activity of the heterogeneous catalysts in the Heck reaction. Another limitation concerns the determination of palladium species dissolved but retained in the zeolite cages which cannot be detected by this procedure.

The results obtained (Fig. 2) show that the leaching of active species in the bulk solution is much more pronounced with Y-type zeolites than with Mordenite type zeolites. For the latter it can be neglected since the differences observed between the two determinations are in the error limit of the analytical GLC. This observation can be rationalised by the effect due to
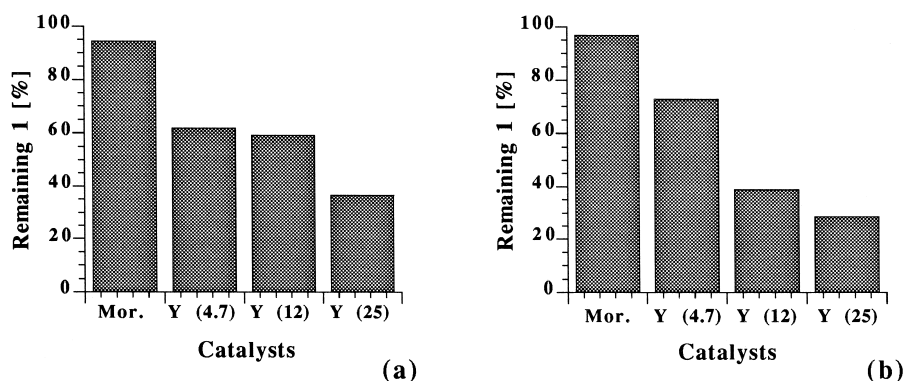

Fig. 2. Leaching of active species in the heterogeneously catalysed Heck reaction. Remaining p-BrFC$_6$H$_4$ **1** after the reaction are displayed. Zeolites (H-Mordenite and H-Y) were loaded with 7% Pd(0) (a) or Pd(II) species (b).

Table 3
Results obtained for the Heck reaction (Scheme 2) with recovered 7% Pd(II) Mordenites (Na- or H-form) or H-Y zeolites

Entry	Zeolite type	trans-Stilbene 3 [%]	
		First run	Second run
1	Na-Mordenite	89.6 (92.0)	84.8 (80.0) [69.7]
2	H-Mordenite	89.7 (90.8)	87.3 (85.6) [75.8]
3	H-Y, $SiO_2/Al_2O_3 = 4.7$	90.1 (92.0)	86.0 (81.7) [72.4]
4	H-Y, $SiO_2/Al_2O_3 = 12$	90.2 (93.0)	89.2 (88.9) [77.9]
5	H-Y, $SiO_2/Al_2O_3 = 25$	89.8 (91.5)	88.7 (87.7) [79.2]

A comparison with the first run of the catalyst is reported. Product distribution, (GLC-Yields) and [Isolated-Yields] are given ($\Delta_{rel} = \pm 10\%$).

the zeolite structure. Y zeolite has larger supercage windows than Mordenite [27], the aperture of the former could possibly easier passed by large Pd complexes.

For the Y-zeolite, a dependence on the Pd oxidation state and the SiO_2/Al_2O_3 ratio is observed. It is generally admitted that the zeolites with SiO_2/Al_2O_3 ratio greater than 7 have the same acid character, and are classified as acid type zeolites. Pd(II) modified zeolites with a SiO_2/Al_2O_3 ratio of 12 and 25 gave more active species in solution as the zeolite with a SiO_2/Al_2O_3 ratio of 4.7 (a 'more basic' one) [32]. Considering that the Pd(II) species are reduced to Pd(0) at the beginning of the reaction, the results observed can be correlated with an internal stabilisation of the Pd(0) species by the zeolite structure, the more basic one ($SiO_2/Al_2O_3 = 4.7$) leading to more stable catalysts against leaching [33].

3.5. Recovery of the heterogeneous catalysts

An important point concerning the use of heterogeneous catalysts is its life time, particularly for industrial and pharmaceutical applications of the Heck reaction.

After separation and washing, the heterogeneous catalysts were used for the same or similar reactions under the same reaction conditions as for the initial run of the catalyst without any regeneration. The results obtained with Pd(II) modified zeolites for the chosen Heck reaction

are reported in Table 3. Most of the catalysts still showed a high activity. The Pd(0) modified zeolites gave similar results concerning the recovery of the heterogeneous catalysts.

3.6. Variation of the substituent in the aryl bromide educt

In addition to the results obtained with the model reaction (Scheme 2, R = F), experiments have been made using other aryl halides as substrates. The results obtained for the Heck reaction with 10% Pd loaded H-Mordenite are reported in Table 4.

The heterogeneous catalysts showed a high activity towards the Heck reaction of aryl bromides with styrene, also with the 'non-activated' bromobenzene (R = H). The gradation of the aryl bromide conversion is similar to homogeneous catalysis and depends on the activation brought by the substituent in *para*-position. The activated aromatic bromides (i.e., the ones wearing an electron withdrawing group in the *para*-position) gave better results.

In these experiments, no pronounced 'leaching' was found. The results are qualitatively identical to the ones obtained using the *p*-bromofluorobenzene. The recovery of the catalysts was also studied, and the catalysts showed an unchanged activity in the second run. In the case of the Heck reaction of bromobenzene with styrene it was observed that the recovered cata-

Table 4
Results obtained for the Heck reaction (Scheme 2) with 7% Pd(II) or Pd(0) H-Mordenites

Entry	R	Pd Species	trans-Stilbene 3 [%]
1	NO_2	Pd(0)	94.7 (96.2) [87.4]
2	NO_2	Pd(II)	94.7 (93.7) [82.6]
3	CH_3CO	Pd(0)	93.7 (85.5) [79.6]
4	CH_3CO	Pd(II)	93.6 (84.5) [82.9]
5	F	Pd(0)	85.1 (81.5) [72.2]
6	F	Pd(II)	89.7 (90.8) [83.9]
7	H	Pd(0)	51.9 (31.8) [39.2]
8	H	Pd(II)	82.5 (71.5) [71.8]

Products distribution, (GLC-Yields) and [Isolated-Yields] are given ($\Delta_{rel} = \pm 10\%$).

lyst (provided from the Pd(0) loaded zeolites) showed a higher activity than the fresh catalyst (Table 5).

This phenomenon was already mentioned in the literature without explanation [34]. We propose that its origin is a redispersion of the palladium particles under the reaction conditions, leading to a higher dispersed catalyst with a higher activity [35–37]. The relatively low reactivity of the bromobenzene in the Heck reaction allows the observation of this phenomenon, which is not the case with the other aryl halides used in these studies.

3.7. Comparison with homogeneously catalysed Heck reaction

In addition to the experiments reported above, we performed homogeneously catalysed Heck reactions in order to determine the influence of the zeolite (e.g., shape selectivity) in the Heck reaction.

The results reported in Table 6 for the homogeneously and the heterogeneously catalysed Heck reactions did not show an influence of the zeolite used as support for the Pd(II/0) species. Similar yields and selectivities are provided by both which indicate a similar mechanism. At this stage of our studies, we cannot exclude that a homogeneous mechanism occurs for the heterogeneously catalysed Heck reactions, this seems to be even probable. A possible explanation is that the active palladium species are complexes obtained from the dissolution of the palladium particles—present in the zeolite cages—and retained in the zeolite bulk. These

Table 5
Results obtained for the Heck reaction (Scheme 2, R = H) with recovered 7% Pd(0) or Pd(II) H-Mordenites

Entry	Pd species	*trans*-Stilbene **3** [%]	
		First run	Second run
1	Pd(0)	51.9 (31.8)	77.5 (60.9)
2	Pd(II)	82.5 (71.5)	69.0 (49.7)

A comparison with the first run of the catalyst is reported. Product distribution and (GLC-Yields) are given ($\Delta_{rel} = \pm 10\%$).

Table 6
Results obtained for the Heck reaction (Scheme 2, R = F) with homogeneous and heterogeneous catalysts

Entry	Catalyst	**3** [%]	**4** [%]	**5** [%]
1	Pd(OAc)$_2$	83.8 (76.9)	0.9 (0.9)	7.6 (7.4)
2	[Pd(NH$_3$)$_4$]$^{2+}$, 2 Cl$^-$	90.9 (94.0)	0.9 (1.0)	8.1 (8.8)
3	Pd(0)-HY	89.4 (89.6)	0.9 (1.0)	8.2 (8.6)
4	Pd(II)-HY	90.2 (93.0)	1.0 (1.0)	8.4 (9.1)

Pd-zeolite catalysts refer to 7% Pd-species immobilised in HY zeolite with a SiO$_2$/Al$_2$O$_3$ = 12. Product distribution and (GLC-Yields) are given ($\Delta_{rel} = \pm 10\%$).

cannot be detected in the 'leaching' studies described above. They could be stabilised against agglomeration to less (in)active Pd-particles in solution (e.g., by dissolution precipitation (desorption–adsorption) equilibria at the rather high temperatures.

4. Conclusions

Palladium modified zeolites exhibit a high activity towards the Heck reaction of aryl bromides with styrene, using standard reaction conditions. Remarkable are the small amounts of palladium (0.2 mol%) required to perform the heterogeneously catalysed Heck reaction. The catalysts can be easily separated from the reaction mixture (filtration) and reused after washing (without reactivation) without loss in activity. Except for the catalysts based on the Y structure, no remarkable leaching of active species was observed. As for the homogeneous Heck reaction, the electronic nature of the aryl bromide has a dominating effect on the reaction yield. The activated aryl bromides react nearly quantitatively. The results indicate that the activity of the palladium modified zeolites are related to the dispersion of the palladium species, higher dispersions giving higher activities.

Whereas the reaction mechanism of the homogeneously catalysed Heck reaction is today generally accepted [1,2] the mechanism of the heterogeneously catalysed Heck reaction remains unclear. The experiments indicate that

Pd(0) species are the active species (as for the homogeneous systems). The results observed are consistent with an oxidative addition of the aryl bromide to the Pd(0) centre via a S_NAr route. In addition, the identical product distributions (selectivity) in homogeneous and heterogeneous reactions indicate the same reaction mechanism for both. At this stage of the studies, we cannot distinguish between a homogeneous and a heterogeneous mechanism for the heterogeneously catalysed Heck reaction, both taking place in the zeolite cages: the active palladium species could be palladium complexes formed in dissolution–adsorption equilibria of Pd(0/II) particles but retained in the zeolite cages. Current investigations focus on the kinetic and the homogeneous/heterogeneous mechanistic aspect.

Acknowledgements

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