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Heck reactions between aryl halides and olefins catalysed by Pd-complexes entrapped into zeolites NaY

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Abstract

Palladium complexes entrapped into zeolite cages have been prepared and characterised by MAS-NMR. They exhibit a high activity towards the Heck reaction of aryl bromides with olefins for small palladium concentrations (0.1 mol%). The catalysts can be easily separated from the reaction mixture and reused after washing without loss in activity. Except for very large complexes, no limitation to the diffusion of educts in the zeolite cages was observed. As for the homogeneous Heck reaction, the electronic nature of the aryl bromides and the olefins has a dominating effect on the reaction yield and selectivity. The heterogeneous catalysts activate even aryl chlorides under standard reaction conditions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Heck olefination; Zeolite; Palladium; Aryl halides; Heterogeneous catalysis; Entrapped complexes

1. Introduction

The palladium-catalysed carbon–carbon bond formation between aryl halides and olefins (Heck reaction) discovered in 1971 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].

While the use of soluble palladium complexes to promote this reaction is well established (high reactivity and high selectivity) [1,2], homogeneous catalysts are generally connected with problems of separation (purity of the products), recovery and regeneration of the catalysts. Such problems are of importance for industrial applications (large-scale synthesis) where the costs of the catalyst materials are of importance. Although recent advances in the design of homogeneous catalysts have been made, in addition to the separation problems deactivation of the homogeneous catalysts by formation of inactive colloidal species is encountered at the comparatively high reaction temperature [3].

The problems discussed could be principally minimised by a heterogeneously catalysed Heck reaction [4]. However, only sporadic reports have appeared in the last 15 years for the activation of iodo- and bromobenzenes in solution. Anchored Pd-complexes [5], Pd/C, Pd/MO$_x$ [6], Pd/MCM-41 [7] were used. Generally no data have been reported concerning the problem of dissolution of active species (leaching). Recently, we reported a study concerning the activation of aryl bromides by Pd(0) and Pd(II) zeolites for the Heck reaction [8]. Direct activation of chlorobenzenes by heterogeneous systems has been reported, but only under drastic reaction conditions (high temperature, no solvent or participating solvent such as MeOH) [9].

Although, to the best of our knowledge, there is no report about the Heck reaction with Pd-complexes entrapped in zeolites, their use as support should have the following advantages: (1) complexes immobilised in zeolite super-cages should have almost the same activity as the free complexes in solution [10], and (2) the zeolite microstructure (micro-reactor) could help to overcome the problems of leaching using heterogeneous catalysts in solution. In addition, zeolites are capable of stabilising intermediate active species retained in their cavities and combine the shape-selectivity [11].

Here we report for the first time that Pd-complexes partially used in homogeneous catalysis could be immobilised in zeolites to give highly active, selective and

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recoverable heterogeneous catalysts towards the Heck reaction of aryl bromides with olefins. The phenomenon of leaching of active species in the bulk solution has been studied in detail.

2. Results and discussion

2.1. Catalyst preparation

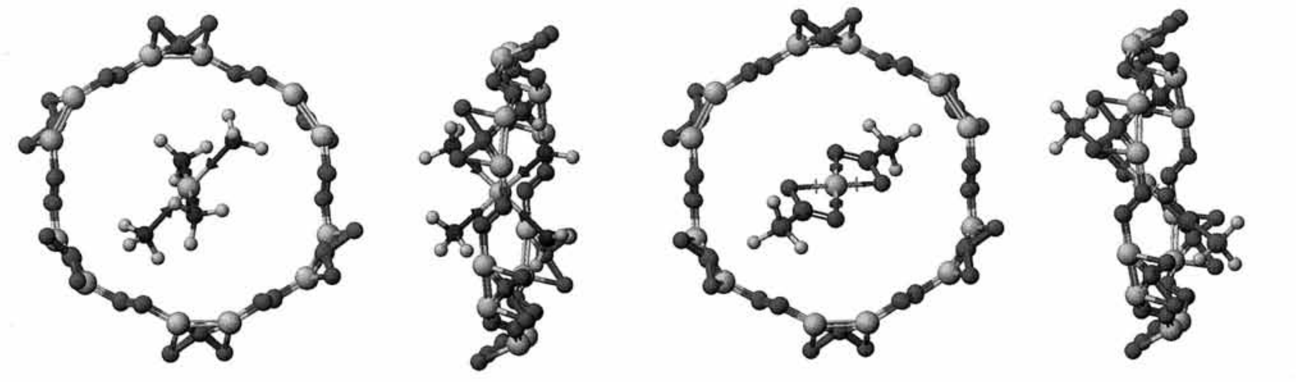
Analogous to the well known ion-exchange process reported for the $[Pd(NH_3)_4]^{2+}$ [12], we prepared the Pd-complex loaded zeolites by immobilisation of the three different complexes: $[Pd(OAc)_2]$, $[Pd(C_3H_5)Cl]_2$ and $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]\}^+$ [2e,13] in the zeolite super-cage.

Because the diameter of the zeolite channels is limited (for the Y zeolite: $\varnothing = 7.4$ Å) [14], we performed molecular modelling calculations in order to check whether the complexes can pass through the zeolite window. The results obtained using the MM2 augmented parameters [15] provided with the CAChe™ software from Oxford Molecular Ltd. [16] are reported in Fig. 1.

As we can deduce from Fig. 1, limitations are encountered for most of the chosen complexes:

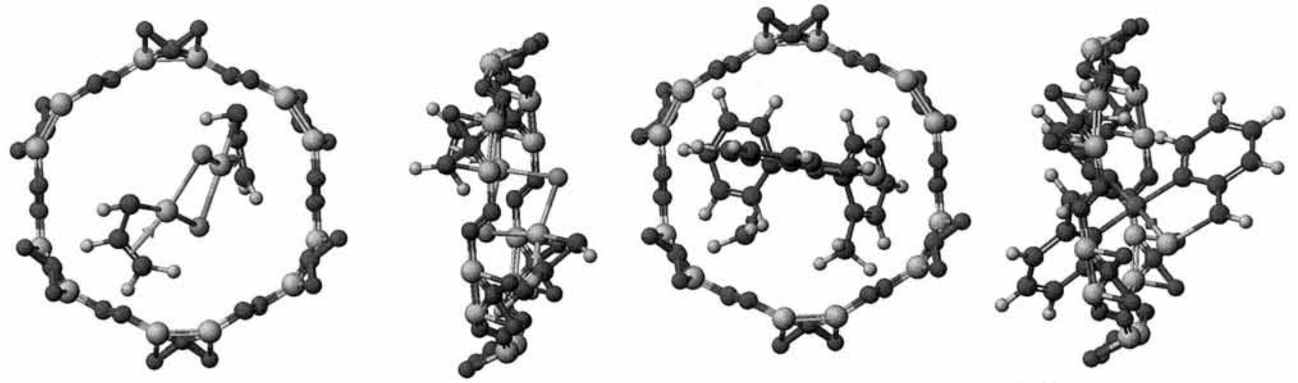
1. Concerning the $[Pd(NH_3)_4]^{2+}$, we did not find any limitation since its small size and its pseudo-spherical geometry allows it to pass through the zeolite window in all directions and for all orientations.
2. Concerning the $[Pd(OAc)_2]$ and $[Pd(C_3H_5)Cl]_2$ complexes we found that according to their geometry, a perpendicular orientation or an orientation with a minimum angle of 56 and 42°, respectively, versus the plane defined by the window is required, in order to pass through the window.
3. Concerning the $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]\}^+$, we found that only a few orientations allow it to pass through the window due to its steric hindrance.

Experimentally, in accordance with these calculations, we found that in order to obtain a reasonable amount of palladium in the zeolite, for the $[Pd(OAc)_2]$ and $[Pd(C_3H_5)Cl]_2$ complexes, 3-day exchange (giving 0.7 and 0.5% Pd-catalyst, respectively) and for $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]\}^+$ 9-day exchange experiments (giving 0.3% Pd-catalyst) are required. The palladium concentrations of the modified zeolites were determined by AAS to be between 0.3 and 1.0% depending on the complexes.



$[Pd(NH_3)_4]^{2+}$ in NaY

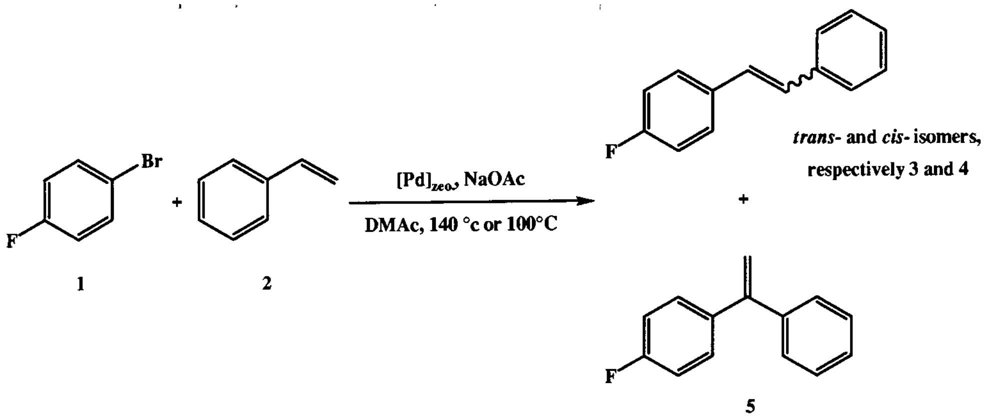
$Pd(OAc)_2$ in NaY



$[Pd(C_3H_5)Cl]_2$ in NaY

Palladacyle in NaY

Fig. 1. Molecular modelling of the Pd-complexes ($[Pd(NH_3)_4]^{2+}$, $[Pd(OAc)_2]$, $[Pd(C_3H_5)Cl]_2$ and the palladacycle $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]\}^+$) in NaY zeolite using the CAChe™ software with the extended MM2 molecular mechanics method.



Scheme 1. Reaction conditions: 10 mmol bromofluorobenzene 1, 15 mmol styrene **2**, 15 mmol NaOAc, 0.1 mol% $[Pd]_{zeo.}$, 8 ml DMAc, 140 or 100°C, 20 h.

MAS-NMR of the Pd-complex loaded zeolites have been recorded and confirmed that the immobilised complexes are intact in the zeolite cages, and gave compatible spectra (^1H, ^{13}C and ^{31}P) to the solution NMR obtained for the corresponding free complexes (see Section 4).

2.2. Catalytic activity studies

2.2.1. Influence of steric hindrance on the Pd-complexes in zeolite cages

We chose the reaction of bromofluorobenzene with styrene as the model reaction (Scheme 1). This reaction gives high yields of Heck product with homogeneous catalysts, thereby allowing the observation of small changes in activity of the catalysts.

The conversion and selectivity obtained for the Pd-complex loaded zeolites (0.1 mol% Pd/aryl bromide **1**) are reported in Table 1 and compared to the results obtained with the corresponding Pd-complexes in bulk solution (i.e. homogeneous catalysis).

In accordance with the molecular modelling results described in Fig. 1 and with the homogeneous catalysis of the same complexes (see below), the results indicate that the catalytic activity of the Pd-loaded zeolites is dependent on the steric hindrance of the complexes. Thus, a higher activity was observed for the $[Pd(NH_3)_4]^{2+}$ complex than for the larger $[Pd(OAc)_2]$ and $[Pd(C_3H_5)Cl]_2$ complexes. Concerning the palladacycle $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]\}^+$ entrapped in zeolite NaY a very low activity was obtained. This dependence of activity is probably due to the steric hindrance created by the complexes in the zeolite super cage, which limit the diffusion of the educts and/or products and the accessibility of the metal centre for the educts. This effect is dramatically enhanced by the large size of the palladacycle for which a low activity was observed.

Table 1 also shows that the activity of the complexes immobilised in zeolite cages is not strongly dependent on the temperature of the reaction (slightly lower yields being observed at 100°C). These small differences could indicate that different active species are formed at the two temperatures, the species generated at 100°C being probably more active (but less stable, see later).

In order to confirm the above interpretations of the catalytic results as a steric effect, it is necessary to compare these results with those of the free Pd-complexes in solution (homogeneous catalysts without zeolite). Table 1 shows that the Pd-complexes immobilised in zeolite have almost the same activity as the free Pd-complex when no steric hindrance dramatically decreases the reaction rate (i.e. as for the palladacycle $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]\}^+$). A comparison of the activity of the free and immobilised $[Pd(OAc)_2]$ and $[Pd(C_3H_5)Cl]_2$ at 100°C show that higher activity for the immobilised complexes is obtained. This is probably due to better stabilisation of the active Pd-species by the zeolite framework.

Table 1
Results obtained for the Heck reaction (Scheme 1) with different Pd-complex loaded NaY [a]

Pd-complex	T (°C)	**3** (%)	**4** (%)	**5** (%)
$[Pd(NH_3)_4]^{2+}$	140	93.0 [89.1] {94.0}	1.0 {1.0}	8.8 {8.8}
	100	94.5 [89.5] {92.2}	0.7 {1.0}	6.7 {8.4}
$[Pd(OAc)_2]$	140	79.2 [68.7] {83.8}	0.9 {0.9}	7.2 {7.6}
	100	57.6 [39.9] {47.6}	0.4 {0.3}	3.9 {3.9}
$[Pd(C_3H_5)Cl]_2$	140	86.3 [78.2] {87.1}	1.0 {0.9}	8.3 {8.4}
	100	74.2 {30.9}	0.5 {0.2}	5.2 {2.1}
Palladacycle	140	3.0 {92.3}	0.1 {1.1}	0.2 {7.9}
	100	1.0 {90.5}	nd {1.0}	nd {8.1}

[a] GLC yields [isolated yields] are given and compared with {GLC yields for homogeneous catalysis} ($\Delta_{rel} = \pm 10\%$).

Table 2
Results obtained for the Heck reaction (Scheme 1) with recovered Pd-complex-loaded NaY [a]

Pd-complex	T (°C)	**3** (%)	
		First run	Recycled
$[Pd(NH_3)_4]^{2+}$	140	93.0	80.9
	100	94.5	1.0
$[Pd(OAc)_2]$	140	79.2	81.2
	100	57.6	17.8
$[Pd(C_3H_5)Cl]_2$	140	86.3	72.0
	100	74.2	1.4

[a] GLC yields are given and compared with the results of the first run of the catalysts ($\Delta_{rel} = \pm 10\%$).

2.2.2. Recovery of the Pd-complex-loaded zeolites

After separation and washing, the heterogeneous catalysts were used for the same reactions under the same reaction conditions as for the initial run of the catalyst without any regeneration. The conversion and selectivity are reported in Table 2.

Table 2 shows that all the complexes used in a first run at 140°C still show a high activity that is comparable to the activity observed for the first run. In contrast, the catalysts used in a first run at 100°C show a lower activity in these experiments (at 100°C).

In order to explain these results, we tried to regenerate the catalysts used in a first run at 100°C. This was done by treating the recovered catalysts at 140°C for 1 h under the reaction conditions.

The results reported in Table 3 show that the regenerated catalysts then show a high activity that is comparable to the activity observed for the recovered catalysts used in a first run at 140°C.

These observations can be rationalised by the generation of different active species at the two temperatures, the species generated at 100°C being irreversibly destroyed during the extraction condition in air while the species generated at 140°C are stable.

Table 3
Results obtained for the Heck reaction (Scheme 1 at $T = 100$°C) with recovered Pd-complex loaded NaY before and after the regeneration [a]

Pd-complex	Reactivation	**3** (%)	
		First run	Recycled
$[Pd(NH_3)_4]^{2+}$	No	94.5	1.0
	Yes	94.5	75.2
$[Pd(OAc)_2]$	No	57.6	17.8
	Yes	57.6	79.8
$[Pd(C_3H_5)Cl]_2$	No	74.2	1.4
	Yes	74.2	75.3

[a] GLC yields are given and compared with the results of the first run of the catalysts ($\Delta_{rel} = \pm 10\%$).

These results can be compared with results we have previously reported for Pd(II) or Pd(0) modified zeolites [9]. These were highly active and recoverable heterogeneous catalysts toward the Heck reaction at 140°C. We postulate that the active Pd-species generated for all of them at 140°C have probably the same structure, probably Pd(0)-particles bound into the zeolite cage.

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

The leaching of active species from heterogeneous catalysts used in solution is a crucial question in order to identify whether the active centres are immobilised in the zeolite framework or dissolved palladium complexes in the homogeneous solution. Thus, we have studied this phenomenon in more detail.

The leaching was studied as follows: the organic phase of a first run was separated from the solid (Pd modified zeolite). New reagents (p-$BrFC_6H_4$ **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 $p BrFC_6H_4$ **1** being set to 100%. This homogeneous reaction mixture was treated as a standard catalytic experiment (100 or 140°C, 20 h). After 20 h reaction time, the composition was determined once more by GLC. The differences observed between the two GLC determinations give qualitative information about the leaching phenomenon.

While this method does not allow an absolute quantification of the palladium species (active and/or inactive) dissolved in the bulk solution by the leaching phenomenon, it gave information concerning the presence of active species in homogeneous solution. This method also gives an idea of the relative influence of these species on the observed activity of the heterogeneous catalysts for the Heck reaction.

The results reported in Fig. 2 show that the leaching phenomenon depends on the temperature of the reaction and on the structure of the Pd-complex immobilised in the zeolite cages.

While the difference between the two determinations stays in the limit error of the analytical GLC, for the $[Pd(NH_3)_4]^{2+}$ a higher leaching is observed at 140°C as at 100°C, for which it was not detected.

For the palladacycle $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5\text{-}CH_2)]\}^+$ no leaching was detected at all, which is in good agreement with a strong immobilisation of the complex in zeolite framework, the homogeneous complex being highly active (cf. Table 1).

Concerning the other complexes, the results are quite different and could not be explained on the basis of temperature and complex structures only. Thus, we did not observe leaching for the immobilised $[Pd(OAc)_2]$ at both reaction temperatures, while we observed a relatively high leaching for the $[Pd(C_3H_5)Cl]_2$ at 140°C. At least the phenomenon could be strongly reduced by the

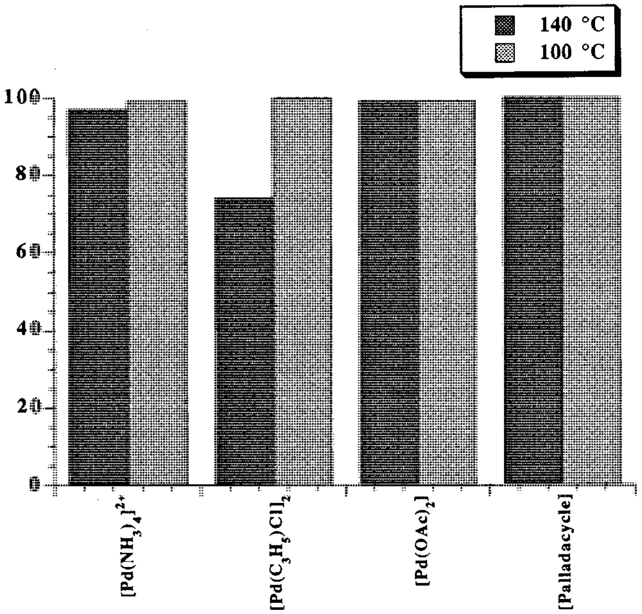


Fig. 2. Leaching of active Pd-species into the bulk solution using the Pd-loaded zeolites as catalysts in solution for the Heck reaction. Reaction conditions: 10 mmol bromofluorobenzene, 15 mmol styrene, 15 mmol NaOAc, 0.1 mol% $[Pd]_{zeo.}$, 8 ml DMAc, 140 or 100°C, 20 h.

use of a lower reaction temperature (i.e. 100°C). To explain these observations, we should consider the relative stability of both complexes under the same reaction conditions. Thus the $[Pd(C_3H_5)Cl]_2$ will decompose quickly at 140°C ($T_{dec.} = 120°C$) [17] whereas the $[Pd(OAc)_2]$ will decompose more slowly ($T_{dec.} = 205°C$) [17] at this temperature, probably leading to higher stabilised Pd-species in the zeolite cages. This is correlated with the results observed at 100°C, where the $[Pd(C_3H_5)Cl]_2$ should be slower decomposed to give more stable Pd-species in the zeolite cage. These arguments also apply to the $[Pd(NH_3)_4]^{2+}$ complex (it decomposes in two steps: $T_{dec._1} = 158°C$, and $T_{dec._2} = 285°C$) [18] entrapped into the NaY, which can explain the slightly better stability of the catalyst obtained at 100°C.

2.3. Kinetic studies

Kinetics of the reaction between p-$BrFC_6H_4$ **1** and the styrene **2** were studied under standard reaction conditions (Scheme 1: $T = 140°C$). Fig. 3 shows that the $[Pd(NH_3)_4]^{2+}$ -loaded NaY is a highly active catalyst for this reaction after a short activation period (ca. 2 min). The selectivity and the activity observed is comparable to the one obtained using standard homogeneous catalysts [1,2].

Of interest was to compare the kinetics obtained with the $[Pd(NH_3)_4]^{2+}$-loaded NaY to the results obtained for the same reaction under the same conditions with Pd(II)- and Pd(0)-loaded Y zeolites [8].

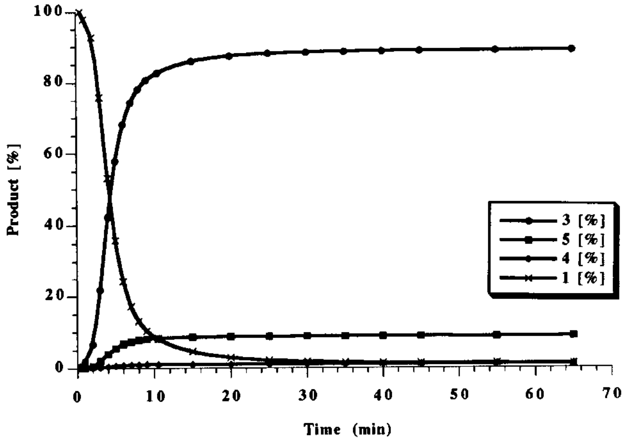


Fig. 3. Kinetic investigations: Conversion of bromofluorobenzene **1** and product percentage (**3**, **4** and **5**) obtained with the $[Pd(NH_3)_4]^{2+}$ loaded NaY for the Heck reaction (Scheme 1).

The results reported in Fig. 4 show that the $[Pd(NH_3)_4]^{2+}$-loaded NaY is much more active as the other Pd-modified Y zeolites. Thus the Heck reaction of p-$BrFC_6H_4$ **1** with styrene **2** is completed after ca. 20 min using $[Pd(NH_3)_4]^{2+}$-loaded NaY where it required ca. 1450 min with Pd(II) modified zeolites. In addition, an induction period of ca. 2 min is observed for the $[Pd(NH_3)_4]^{2+}$-loaded NaY, as it was for the Pd(II) modified zeolite (ca. 4 min) [8]. This period is not observed for the Pd(0)-modified zeolite (Pd(0)-species being Heck active) and corresponds to the delay required for the transformation of the Pd(II) species to Heck active Pd(0) species.

2.4. Variation of the educts

2.4.1. Reaction between aryl bromides and olefins

In order to generalise the results obtained for the heterogeneously catalysed Heck reaction with the

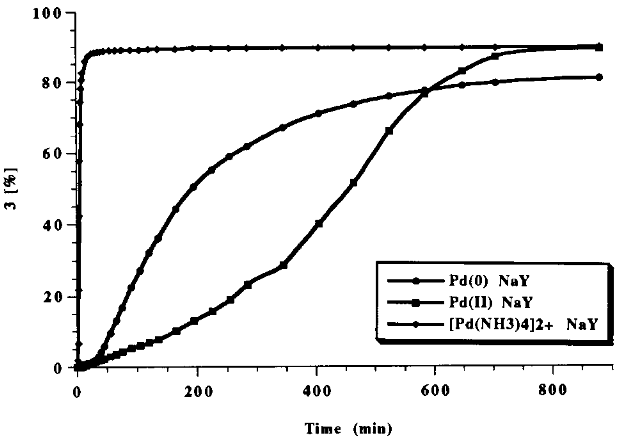
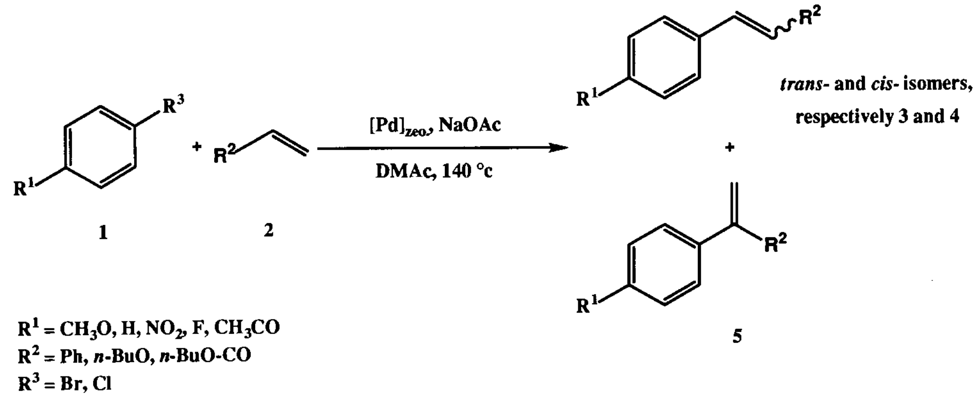


Fig. 4. Kinetic investigations: comparison of the activity of different Pd-species loaded into the zeolites. Percentage of the product **3** obtained with the $[Pd(NH_3)_4]^{2+}$-, Pd(II)- and Pd(0)-loaded NaY for the Heck reaction (Scheme 1).



Scheme 2. Reaction conditions: 10 mmol aryl halide 1, 15 mmol olefin **2**, 15 mmol NaOAc, 0.1 mol% $[Pd]_{zeo.}$, 8 ml DMAc, 140°C, 20 h.

model reaction (Scheme 2), experiments have been carried out using both the aryl halides and olefins as substrates using the $[Pd(NH_3)_4]^{2+}$-loaded NaY catalyst (Scheme 2).

The results reported in Table 4 show that the heterogeneous catalyst has a high activity toward the activation of aryl bromides also for the non-activated bromo-anisole ($R^1 = CH_3O$, $R^3 = Br$). Concerning the variation of the olefins, as expected, the electron-poor olefins ($R^2 = Ph$, *n*-BuO–CO) gave better yields than the electron rich olefins ($R^2 =$ *n*-BuO). The gradation of the aryl bromide conversion is similar to homogeneous catalysis and depends on the activation of the aryl bromides by a *para*-substituent and the electron density of the olefins in the π-bond.

In addition to these experiments, kinetic studies have been performed for the reaction of aryl bromides ($R^1 = F$, H and OCH_3, $R^3 = Br$) and styrene ($R^2 = Ph$) using the $[Pd(NH_3)_4]^{2+}$-loaded NaY (Fig. 5).

The results reported in Fig. 5 show that the $[Pd(NH_3)_4]^{2+}$-loaded NaY is a highly active heterogeneous catalyst for the Heck reaction, including the non-activated bromobenzene and the 'deactivated' bromo-anisole. As reported above, an initiation period of ca. 2–5 min is observed before the reaction starts, corresponding to the transformation of the immobilised complex to active Pd(0) species. These results are comparable to the one reported for the homogeneously catalysed Heck reaction [2].

Table 4
Results obtained for the Heck reaction (Scheme 2, $T = 140°C$) with different aryl halides and olefins using the $[Pd(NH_3)_4]^{2+}$ loaded NaY [a]

R^1	R^2	**3** (%)	**4** (%)	**5** (%)
H	Ph	84.9 [77.8]	0.7	6.5
F	Ph	93.0 [89.1]	1.0	8.8
NO_2	Ph	94.8 [89.8]	1.1	4.1
CH_3O	Ph	81.2 [75.8]	9.5	9.5
H	*n*-BuO	25.7	20.4	12.4
H	CH_3O–CO	91.0 [69.4]	0.5	0.4
F	CH_3O–CO	93.2 [72.6]	0.7	0.6

[a] GLC yields and [isolated yields] are given ($\Delta_{rel} = \pm 10\%$).

2.4.2. *Activation of aryl chlorides*

Another important issue concerning the heterogeneously catalysed Heck reaction is the possibility to activate the industrially more interesting aryl chlorides. In order to examine this possibility, we studied the reaction between chloroacetophenone ($R^1 = CH_3CO$, $R^3 = Cl$; see Scheme 2) and styrene ($R^2 = Ph$) using the $[Pd(NH_3)_4]^{2+}$-loaded NaY as heterogeneous catalyst.

As expected, the results reported in Table 5 show that the activation of aryl chlorides required a higher temperature as the bromo-derivatives. This is connected with the halogen–carbon bond energy, which was calculated for the bromoacetophenone (ca. 80.5 kcal mol^{-1}) [19] and the chloroacetophenone (ca. 96 kcal mol^{-1}) [19]. As it was already mentioned in the literature, an interesting salt effect was observed with *t*-Bu_4NBr [20], which gave a benefit for this reaction, but is accompanied in this experiment by a parallel dehalogenation reaction leading to the formation of acetophenone in 8.3% yield.

3. Conclusions

Palladium-complex-loaded zeolites exhibit a high activity towards the Heck reaction of aryl bromides with olefins, using standard reactions conditions. Remarkable are the small amounts of palladium (0.1 mol%) required to perform the heterogeneous catalysed Heck reaction. As for the homogeneous Heck reaction, the electronic nature of the aryl bromides and the olefins has a dominating effect on the reaction yield and selectivity. The activated aryl bromides and the electron poor olefins ($R^2 = Ph$, *n*-BuO–CO) almost react quantitatively. The catalysts can be easily separated from the reaction mixture (filtration) and reused after washing. Depending of the reaction temperature, some catalysts

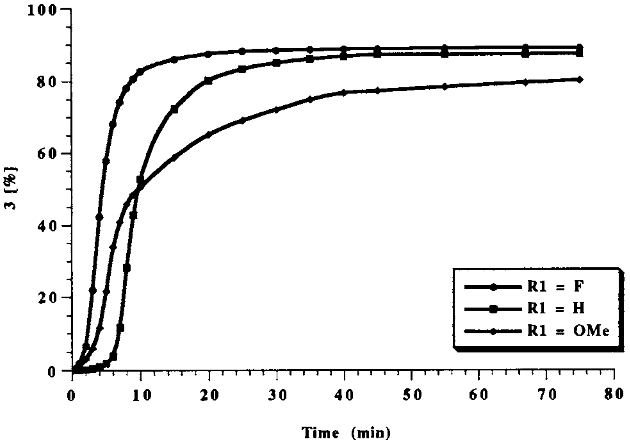


Fig. 5. Kinetic investigations: comparison of the activity of the $[Pd(NH_3)_4]^{2+}$-loaded NaY for the Heck reaction (Scheme 2, $R^1 = H$, F or CH_3O, $R^2 = Ph$ and $R^3 = Br$). Percentages of the product **3** are reported.

were deactivated during the extraction. However, active species could be regenerated using an easy procedure. Except for one catalyst (the $[Pd(C_3H_5)Cl]_2$-loaded NaY used at 140°C), no remarkable leaching was observed for the Pd-complex-loaded zeolites. The investigations concerning the leaching phenomenon showed that a more stable catalyst could be obtained by generating the Pd-active species at a lower temperature in the case of the $[Pd(C_3H_5)Cl]_2$ complex. The stability of the Pd-active species against leaching seems to be correlated to the temperature of decomposition (in the starting period) of the immobilised Pd-complexes in the zeolite cages, a too quick decomposition leading to stronger leaching.

Except for large complexes (i.e. the palladacycle $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]\}^+$), no limitation to the diffusion of educts in the zeolite cages was observed for the reaction. The kinetics performed with the $[Pd(NH_3)_4]^{2+}$-loaded NaY show that the heterogeneous catalysts have a comparable activity to the homogeneous catalysts, the complete conversion of the aryl bromides being of ca. 20 min, including the non activated derivatives. For the first time, we report a direct activation of aryl chlorides using a heterogeneous catalyst, under standard reaction conditions. No undesired reactions (i.e. strong dehalogenation of the aryl chlorides, biphenyl derivatives or reacting solvent) were observed.

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 [21]). 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 propose that a homogeneous mechanism take place in the zeolite cage for the heterogeneously catalysed Heck reaction using Pd-complexes entrapped in zeolites. The active palladium species could be palladium complexes formed in situ by decomposition of the entrapped Pd-complexes, these complexes co-exist probably with adsorbed entities by a dissolution–adsorption equilibrium of Pd(0/II) species but are retained in the zeolite cages. Current investigations focus on the kinetic and the homogeneous/heterogeneous mechanistic aspect.

Table 5
Results obtained for the Heck reaction (Scheme 2) with chloroacetophenone and styrene using the $[Pd(NH_3)_4]^{2+}$-loaded NaY in the presence and absence of a co-catalyst [a]

T (°C)	Co-catalyst	**3** (%)	**4** (%)	**5** (%)
140	No	0.3	nd	0.3
170	No	44.1 [31.2]	1.2	3.3
170	Yes	59.2 [38.1]	1.0	2.0

[a] GLC yields and [isolated yields] are given ($\Delta_{rel} = \pm 10\%$).

4. 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. THF and DMF was freshly distilled under argon over sodium from purple benzophenone ketyl before use. The zeolite NaY was purchased from Sigma-Aldrich Chemical (LZ-Z-52) and dried under 5×10^{-2} mmHg at 120°C for 48 h before use in the synthesis of catalysts 2–4. All other chemicals (organic reagents and solvent) were deaerated by an argon flow before they were used. The Pd-loaded zeolites were stored after drying under Ar atmosphere.

Solution NMR spectra of the organic products 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).

Solid-state ^{1}H-, ^{13}C-, and ^{31}P-MAS-NMR spectra of the exchanged zeolites were recorded on a Bruker MSL 300 spectrometer operating at a field strength of 7.05 T. For the ^{1}H- and ^{13}C-MAS-NMR spectra, ca. 300 mg of the sample were packed into 4 mm ZrO_2 Bruker rotors with Kel-F caps. For the ^{31}P spectrum a 7 mm ZrO_2 Bruker rotor with ca. 1 g of sample was used. ^{1}H- and

^{13}C-NMR shifts are referenced to an external sample of adamantane; the proton signal is set to 2 ppm and the low-frequency signal of the ^{13}C spectrum to 29.472 ppm relative to TMS. The ^{31}P-MAS-NMR spectrum is referenced externally to solid $NH_4H_2PO_4$ with a signal shift of 1.11 ppm relative to 85% H_3PO_4. ^{1}H-MAS-NMR spectra were recorded at a sample spinning speed of 15 kHz. ^{13}C-CP-MAS-NMR spectrum was recorded at a spinning speed of 8 kHz, using high-power proton decoupling, with a recycle time of 8 s and a contact time of 5 ms. The ^{31}P-MAS-NMR spectrum was obtained at a sample spinning speed of 7 kHz.

Gas–liquid chromatograms were performed on an HP 6890 series chromatograph equipped with a FID detector and a HP-1 column (cross-linked methylsiloxane, 30 m × 0.25 mm × 0.25 mm film thickness).

The absolute palladium content of the catalysts was determined by AAS for the Pd-complex-loaded zeolites after drying and calcination (in order to remove all organic material) from a solution obtained by treatment with a mixture of HBF_4, HNO_3 and HCl in a Teflon reactor at 180°C.

4.1. Preparation of the catalysts

4.1.1. Preparation of the $[Pd(NH_3)_4]$-modified zeolite (cat. 1)

A 0.1 M ammoniac solution of $[Pd(NH_3)_4]Cl_2$ prepared from $PdCl_2$ and a commercial ammoniac solution (0.95 ml g^{-1} zeolite, ca. 1% Pd in the final catalyst) was added drop wise to a suspension of the zeolite NaY in bidistilled water (100 ml g^{-1} zeolite). The mixture was stirred for 24 h at room temperature (r.t.) and the exchanged zeolite was filtered and washed until no trace of chloride was detected in the filtrate ($AgNO_3$ test). Then the zeolite was allowed to dry at r.t. to give the entrapped $[Pd(NH_3)_4]^{2+}$ zeolite as a slightly yellow material. The AAS gave $1.0 \pm 0.2\%$ Pd (w/w).

4.1.2. Preparation of the $[Pd(OAc)_2]$-modified zeolite [cat. 2]

A solution of the $Pd(OAc)_2$ (110.2 mg, 0.47 mmol, ca. 1% Pd in the final catalyst) in THF was added drop wise to a suspension of the zeolite NaY (4.95 g) in THF (20 ml g^{-1} zeolite). The mixture was stirred for 3 days at r.t. and the $[Pd(OAc)_2]$-loaded zeolite was filtered and washed with THF until no trace of non-immobilised complex was detected in the filtrate. Then the zeolite was allowed to dry at r.t. to give the entrapped $[Pd(OAc)_2]$ zeolite as a slightly brown material. The AAS gave $0.7 \pm 0.2\%$ Pd (w/w).

MAS-NMR: ^{1}H-NMR, ppm: 2.10 ($C\underline{H}_3CO$).

MAS-NMR: ^{13}C-NMR, ppm: 186.84 ($CH_3\underline{C}O$); 23.04 ($\underline{C}H_3CO$).

4.1.3. Preparation of the $[Pd(C_3H_5)Cl]_2$-modified zeolite [cat. 3]

A solution of the $[Pd(C_3H_5)Cl]_2$ (88.4 mg, 0.47 mmol, ca. 1% Pd in the final catalyst) in THF was added drop wise to a suspension of the zeolite NaY (4.95 g) in THF (20 ml g^{-1} zeolite). The mixture was stirred for 3 days at r.t. and the $[Pd(C_3H_5)Cl]_2$-loaded zeolite was filtered and washed with THF until no trace of non-immobilised complex was detected in the filtrate. Then the zeolite was allowed to dry at r.t. to give the entrapped $[Pd(C_3H_5)Cl]_2$ zeolite as a yellow material. The AAS gave $0.5 \pm 0.1\%$ Pd (w/w).

MAS-NMR: ^{1}H-NMR, ppm: 2.14 ($C\underline{H}^1H^2CHC\underline{H}^1H^2$); 4.03 ($CH^1\underline{H}^2CHCH^1\underline{H}^2$); 7.15 ($CH^1H^2C\underline{H}CH^1H^2$).

MAS-NMR: ^{13}C-NMR, ppm: 107.15 ($CH_2\underline{C}HCH_2$); 69.07 ($\underline{C}H_2CH\underline{C}H_2$).

4.1.4. Preparation of the $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]\}^+$-modified zeolite [cat. 4]

A solution of the $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]\}^+$, NO_3^- (222.8 mg, 0.47 mmol, ca. 1% Pd in the final catalyst) in DMF was added drop wise to a suspension of the zeolite NaY (4.95 g) in THF (20 ml g^{-1} zeolite). The mixture was stirred for 9 days at r.t. and the $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]\}^+$-loaded zeolite was filtered and washed with a mixture DMF/THF (2:3) until no trace of non-immobilised complex was detected in the filtrate. Then the zeolite was washed with THF and allowed to dry at r.t. under vacuum to give the entrapped $\{Pd[P(o\text{-}C_6H_5CH_3)_2(C_6H_5CH_2)]\}^+$ zeolite as a yellow material. The AAS gave $0.3 \pm 0.1\%$ Pd (w/w).

MAS-NMR: ^{31}H-NMR, ppm: 33.9 (P).

4.2. Catalytic activity

Catalytic reactions were carried out in pressure tubes under argon. The qualitative and quantitative analysis of the reactants and the products was made by GLC. Conversion and selectivity are represented by product distribution (= relative area of GLC signals), and GLC yields are 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. The catalysts were transferred under Ar.

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

A total of 10 mmol of aryl halide, 15 mmol of olefin, 15 mmol of NaOAc and 0.1 mol% of Pd (as heterogeneous catalysts, the amount in g of catalysts depending on the palladium concentration) was introduced in a pressure tube under argon. A total of 8 ml of solvent (DMAc p.a. previously deaerated) was 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 100 or 140°C for 20 h with vigorous stirring and then cooled to r.t. 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 CH_2Cl_2 in order to remove adsorbed organic substrates and dried at r.t.

4.2.2. *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 olefin, 15 mmol of NaOAc and well homogenised. GLC analysis of the composition of the mixture was carried out before the reactor was placed in a pre-heated oil bath at 100 or 140°C for 20 h with vigorous stirring. After the reaction, the reactor was cooled to r.t. 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.

4.2.3. *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-constant pressure (130 kPa): 2 min at 100°C, heating at 15°C min^{-1} up to 170°C, 2 min at 170°C, heating at 35°C min^{-1} up to 240°C, 10 min at 240°C, heating at 50°C min^{-1} up to 270°C and 2 min at 270°C.

4.2.4. *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 pentane (8 ml) was added. 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%.

4.2.4.1. Data for $R = H$. M.p.: 118°C, white plates.

^{1}H-NMR, $CDCl_3$, 400.13 MHz: 7.64 (d, $^3J = 7.0$ Hz, 4H, *ortho*-vinyl, $C_6\underline{H}_5$); 7.48 (pseudo-t, $^3J = 7.5$ Hz, 4H, *meta*-vinyl, $C_6\underline{H}_5$); 7.39 (pseudo-t, $^3J = 7.0$ Hz, 2H, *para*-vinyl, $C_6\underline{H}_5$); 7.24 (s, 2H, $C\underline{H}$-vinyl).

^{13}C-NMR, $CDCl_3$, 400.13 MHz: 137.28 (C-vinyl-$\underline{C}_6H_5$); 128.63 (*meta*-vinyl-$\underline{C}_6H_5$); 128.48 ($\underline{C}$H-vinyllic); 127.56 (*para*-vinyl-$\underline{C}_6H_5$); 126.48 (*ortho*-vinyl-$\underline{C}_6H_5$).

$C_{14}H_{12}$, Anal. [Found (Calc.)]: C 92.01 (93.29), H 6.64 (6.71).

4.2.4.2. Data for $R = F$. M.p.: 122°C, white plates.

^{1}H-NMR, $CDCl_3$, 400.13 MHz: 7.35–7.40 (m, 4H, *ortho*-vinyl, $C_6\underline{H}_4F$ and *ortho*-vinyl, $C_6\underline{H}_5$); 7.26 (pseudo-t, 2H, *meta*-vinyl, $C_6\underline{H}_5$); 7.16(m, 1H, *para*-vinyl, $C_6\underline{H}_5$); 6.92-6.96 (m, 4H, *ortho*-F, $C_6\underline{H}_4F$ and $C\underline{H}$-vinyl).

^{13}C-NMR, $CDCl_3$, 400.13 MHz: 161.06 (C–F, $\underline{C}_6H_4F$); 137.13 (C-vinyl-$\underline{C}_6H_5$); 133.50 (C-vinyl-$\underline{C}_6H_4F$); 128.67 (*meta*-vinyl-$\underline{C}_6H_5$); 128.45 and 128.46 (*ortho*-vinyl-$\underline{C}_6H_4F$); 127.99 and 127.92 ($\underline{C}$H-vinyllic); 127.44 (*para*-vinyl-$\underline{C}_6H_5$); 126.42 (*ortho*-vinyl-$\underline{C}_6H_5$); 115.68 and 115.47 (*meta*-vinyl-$\underline{C}_6H_4F$).

$C_{14}H_{11}F$, mol. wt.: 198.24, MS: m/z (%): [M^+] 198.2 (100), isotopic distribution: 198.2 (100) and 199.2 (11.6). Anal. [Found (Calc.)]: C 84.65 (84.82), H 5.68 (5.59).

4.2.4.3. Data for $R = NO_2$. M.p.: 107°C, yellow plates.

^{1}H-NMR, $CDCl_3$, 400.13 MHz: 8.15 (d, $^3J = 9.0$ Hz, 2H, *ortho*-NO_2, $C_6\underline{H}_4NO_2$); 7.57 (d, $^3J = 9.0$ Hz, 2H, *ortho*-vinyl, $C_6\underline{H}_4NO_2$); 7.50 (d, $^3J = 7.5$ Hz, 2H, *ortho*-vinyl, $C_6\underline{H}_5$); 7.35 (pseudo-t, $^3J = 7.0$ Hz, 2H, *meta*-vinyl, $C_6\underline{H}_5$); 7.16 (pseudo-q, $^3J = 7.0$ Hz, 1H, *para*-vinyl, $C_6\underline{H}_5$); 7.21 (d, $^3J = 16.6$ Hz, 1H, $C\underline{H}$-vinyl); 7.08 (d, $^3J = 16.6$ Hz, 1H, $C\underline{H}$-vinyl).

^{13}C-NMR, $CDCl_3$, 400.13 MHz: 146.47 (C–NO_2, $\underline{C}_6H_4NO_2$); 143.64 (C-vinyl-$\underline{C}_6H_4NO_2$); 135.93 (C-vinyl-$\underline{C}_6H_5$); 133.07 (*meta*-vinyl-$\underline{C}_6H_5$); 128.65 (*ortho*-vinyl-$\underline{C}_6H_4NO_2$); 128.60 (*para*-vinyl-$\underline{C}_6H_5$); 126.80 and 126.64 ($\underline{C}$H-vinyllic);126.00 (*ortho*-vinyl-$\underline{C}_6H_5$); 123.85 (*meta*-vinyl-$\underline{C}_6H_4NO_2$).

$C_{14}H_{11}NO_2$, mol. wt.: 225.24, MS: m/z (%): [M^+] 225.3 (100) [$M^+ - NO_2$] 179.2 (21) [$M^+ - NO_2 - H$] 178.2 (56), isotopic distribution: 225.3 (100) and 226.3 (13.4) 227.3 (1.8). Anal. [Found (Calc.)]: C 73.89 (74.65), H 5.02 (4.92), N 6.32 (6.22).

4.2.4.4. Data for $R = CH_3O$. M.p.: 130°C, light yellow plates.

^{1}H-NMR, $CDCl_3$, 400.13 MHz: 7.55 (d, $^3J = 7.04$ Hz, 2H, *ortho*-vinyl, $C_6\underline{H}_5$); 7.51 (d, $^3J = 9.04$ Hz, 2H, *ortho*-vinyl, $C_6\underline{H}_4OCH_3$); 7.41 (pseudo-t, $^3J = 7.04$ Hz, 2H, *meta*-vinyl, $C_6\underline{H}_5$); 7.32 (pseudo-t, $^3J = 7.00$ Hz, 1H, *para*-vinyl, $C_6\underline{H}_5$); 7.15 (d, $^3J = 16.6$ Hz, 1H, $C\underline{H}$-vinyl); 7.06 (d, $^3J = 16.6$ Hz, 1H, $C\underline{H}$-vinyl); 6.95 (d,

$^3J = 8.9$ Hz, 2H, *ortho*-OCH_3, $C_6\underline{H}_4OCH_3$); 3.86 (s, 3H, $C\underline{H}_3O$).

^{13}C-NMR, $CDCl_3$, 400.13 MHz: 159.20 (C–OCH_3, $\underline{C}_6H_4OCH_3$); 137.43 (C-vinyl-$\underline{C}_6H_5$); 130.00 (C-vinyl-$\underline{C}_6H_4OCH_3$); 128.53 (*meta*-vinyl-$\underline{C}_6H_5$); 128.10 ($\underline{C}$H-vinyllic-C_6H_5); 127.62 (*ortho*-vinyl-$\underline{C}_6H_4OCH_3$); 127.09 ($\underline{C}$H-vinyllic-, $C_6H_4OCH_3$); 126.48 (*para*-vinyl-$\underline{C}_6H_5$); 126.16 (*ortho*-vinyl-$\underline{C}_6H_5$); 114.02 (*meta*-vinyl-$\underline{C}_6H_4OCH_3$); 55.15 ($\underline{C}H_3O$).

$C_{15}H_{14}O$, mol. wt.: 210.27, MS: m/z (%): [M^+] 210.3 (100) [$M^+ - CH_3$] 195.2 (19) [$M^+ - CH_3O$] 179.2 (10). Anal. [Found (Calc.)]: C 85.42 (85.68), H 6.75 (6.71).

4.2.5. Purification of the styrene derivative 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 distillate under 5×10^{-2} mmHg to give the styrene derivative **3** as a colourless oil. The purity of the product was estimated by GLC to be $\geq 99.8\%$.

4.2.5.1. Data for $R = F$, $Eb_{0.05}$. M.p.: 128°C

^{1}H-NMR, $CDCl_3$, 400.13 MHz: 7.91 (d, $^3J = 14.6$ Hz, 1H, C$\underline{H}$-vinyl, C_6H_4F); 7.33 (d, $^3J = 8.05$ Hz, 2H, *ortho*-vinyl, $C_6\underline{H}_4F$); 6.98 (d, $^3J = 8.05$ Hz, 2H, *meta*-vinyl, $C_6\underline{H}_4F$); 6.23 (d, $^3J = 14.6$ Hz, 1H, C$\underline{H}$-vinyl, CO); 4.39 (t, $^3J = 7.0$ Hz, 2H, $C\underline{H}_2O$); 2.49 (pseudo-quintet, $^3J = 7.0$ Hz, 2H, $C\underline{H}_2CH_2O$); 1.23 (pseudo-sextet, $^3J = 7.0$ Hz and $^3J = 6.65$ Hz, 2H, $C\underline{H}_2CH_3$); 0.72 (t, $^3J = 6.65$ Hz, 3H, $CH_2C\underline{H}_3$).

^{13}C-NMR, $CDCl_3$, 400.13 MHz: 174.52 ($\underline{C}$O); 160.18 (C–F, $\underline{C}_6H_4F$); 141.68 ($\underline{C}$H-vinyllic-, C_6H_4F); 131.76 (C-vinyl-$\underline{C}_6H_4F$); 127.62 (*ortho*-vinyl-$\underline{C}_6H_4F$); 127.33 ($\underline{C}$H-vinyllic-CO); 112.49 (*meta*-vinyl-$\underline{C}_6H_4F$); 68.15 ($\underline{C}H_2O$); 32.28 ($\underline{C}H_2CH_2O$); 19.31 ($\underline{C}H_2CH_3$); 13.71 ($CH_2\underline{C}H_3$).

$C_{13}H_{15}FO_2$, mol. wt.: 222.26, MS: m/z (%): [M^+] 222.3 (100) [$M^+ - C_4H_9O$] 149.3 (22) [$M^+ - C_4H_9O -$ CO] 121.3 (42) Anal. [Found (Calc.)]: C 69.82 (70.25), H 6.75 (6.80).

4.2.5.2. Data for $R = H$, $Eb_{0.05}$. M.p.: 116°C

^{1}H-NMR, $CDCl_3$, 400.13 MHz: 7.91 (d, $^3J = 14.6$ Hz, 1H, C$\underline{H}$-vinyl, C_6H_5); 7.27 (m, 5H, $C_6\underline{H}_5$); 6.23 (d, $^3J = 14.6$ Hz, 1H, C$\underline{H}$-vinyl, CO); 4.39 (t, $^3J = 7.0$ Hz, 2H, $C\underline{H}_2O$); 2.49 (pseudo-quintet, $^3J = 7.0$ Hz, 2H, $C\underline{H}_2CH_2O$); 1.23 (pseudo-sextet, $^3J = 7.0$ Hz and $^3J = 6.65$ Hz, 2H, $C\underline{H}_2CH_3$); 0.72 (t, $^3J = 6.65$ Hz, 3H, $CH_2C\underline{H}_3$).

^{13}C-NMR, $CDCl_3$, 400.13 MHz: 174.52 ($\underline{C}$O); 141.68 ($\underline{C}$H-vinyllic-, C_6H_5); 131.52 (C-vinyl-$\underline{C}_6H_5$); 127.33 ($\underline{C}$H-vinyllic-CO); 126.71 (*ortho*-vinyl-$\underline{C}_6H_5$); 126.72 (*meta*-vinyl-$\underline{C}_6H_5$); 125.12 (*para*-vinyl-$\underline{C}$6H5); 68.15 ($\underline{C}H_2O$); 32.28 ($\underline{C}H_2CH_2O$); 19.31 ($\underline{C}H_2CH_3$); 13.71 ($CH_2\underline{C}H_3$).

$C_{13}H_{16}O_2$, mol. wt.: 204.26, MS: m/z (%): [M^+] 204.3 (100) [$M^+ - C_4H_9O$] 131.3 (22) [$M^+ - C_4H_9O - CO$] 103.3 (42) Anal. [Found (Calc.)]: C 75.96 (76.44), H 7.81 (7.90).

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