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Heck Reaction Catalyzed by Pd-Modified Zeolites

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Abstract: [Pd]-exchanged NaY zeolites have been prepared, characterized, and applied for the first time for catalytic carbon−carbon coupling reactions. The catalysts exhibit a high activity and selectivity toward the Heck reaction of aryl bromides with olefins for small palladium concentrations ($\leq$0.1 mol % of Pd). The catalysts can easily be separated from the reaction mixture and reused after washing without loss in activity. No limitation to the diffusion of adducts in the zeolite cages was observed (for linear alkenes). The electronic nature of the aryl bromides and the olefins has a dominating effect on the reaction yield and selectivity. The heterogeneous catalysts quantitatively convert all types of all aryl bromide (complete conversion of bromobenzene within 30 min) and activated aryl chlorides under standard reaction conditions. Product form selectivity is observed in the Heck reaction with cyclic olefins.

Introduction

The Heck reaction, a palladium-catalyzed carbon−carbon bond formation between aryl halides and olefins, became an excellent tool for the synthesis of elaborated styrene derivatives due to its tolerance for a wide variety of functional groups on both reactants[1] and the broad availability of aryl bromides and chlorides.

In the past few years, the development of new highly active soluble Pd complexes allowed the activation and conversion of aryl chlorides,[1,2] which are less reactive than bromides and iodides. Regarding industrial applications, however, these catalysts are expensive (Pd, phosphanes, or special ligand systems). Few experiments address the separation of the catalyst from the reaction mixture and their reuse. In addition to the separation problems, deactivation of the homogeneous catalysts by formation of less active or inactive colloidal Pd species is often encountered at the comparatively high reaction temperature.[3]

Attempts were made to overcome the problems concerning thermal stability (high reaction temperatures), separation, and recovery of the Pd complexes by the use of heterogeneous palladium systems.[4] Polymer-supported Pd complexes were used for the activation of aryl iodides (and bromides) by several groups.[5] Pd on carbon and Pd on different metal oxides were found to be suitable catalysts for the conversion of aryl iodides and bromides.[6] More recently, Pd particles supported on mesoporous silica were successfully applied for the activation of aryl bromides.[7] Activation of chlorobenzenes has been reported, but only under drastic reaction conditions (high temperature, no solvent or reacting solvent such as MeOH).[7,8]

Few investigations correlated the Pd dispersion and activity (conversion, reaction yield).[6] Stabilized Pd colloids can catalyze the Heck reaction of aryl iodides (and partially bromides).[9] Very recent studies demonstrate that, for phosphane or ligand free Pd catalyst systems based on simple Pd salts, in situ formed nanometer scale palladium colloids act as catalyst in the Heck reaction.[9] In general, however, it seems to be not yet clear whether the Heck reaction catalyzed by supported Pd catalysts is due to homogeneous (resolved Pd species) or heterogeneous processes.

Very recently, we reported the first heterogeneous Pd-catalyzed Heck reaction using zeolites as catalyst supports.[10]

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The choice of a zeolite as support was motivated by observations that complexes immobilized in zeolite supercages have almost the same activity as the free complexes in solution[11] and because in this manner a very high palladium dispersion can be achieved. It has been reported that molecules or small metal particles immobilized in zeolite cavities are stable.[11,12] In addition, the zeolite microstructure could help to overcome the problems of leaching present with heterogeneous catalysts in solution. Zeolites are capable of stabilizing intermediate active species in their cavities and of controlling the reaction pathway via shape-selectivity.[12] Corresponding effects could be expected from the similar size of the zeolite pores and the molecules involved (catalyst precursors, adducts and products). For practical applications, the separation of Pd/zeolites by filtration is expected to be easier and faster than, for example, high surface area metal oxides due to the larger zeolite grain size.

The present paper demonstrates that this new approach allowed us to prepare the most active heterogeneous palladium catalysts for the Heck reaction of aryl bromides with olefins. The best catalysts also induced reaction with activated aryl chlorides with significant yields. The paper also addresses a number of important and interesting aspects of the catalytic reaction such as the influence of preparation and treatment of the catalysts, activity and selectivity for a variety of substituents at the aryl halide and alkene, kinetic studies, leaching of Pd species, and recovery and reuse of the catalysts.

Results and Discussions

Catalysts Preparation. To obtain highly active heterogeneous Heck catalysts, in particular of different Pd dispersion, we prepared several "Pd"-exchanged zeolites by immobilization of different Pd species: Pd particles ([Pd(0)]), ionic species ([Pd(II)] and $[Pd(NH_3)_4]^{2+}$), and neutral complexes ($[Pd(OAc)_2]$ and $[Pd(C_3H_5)Cl]_2$). The catalysts loaded with [Pd(0)], [Pd(II)], and $[Pd(NH_3)_4]^{2+}$ were prepared according to the literature[13] by ion exchange of NaY zeolite, using a 0.1 M aqueous solution of $[Pd(NH_3)_4]^{2+}$and $2Cl^-$. After a period of 24 h, $[Pd(NH_3)_4]^{2+}$−NaY was obtained. Calcination at 500 °C under pure O_2 (180 mL/min) of the exchanged $[Pd(NH_3)_4]^{2+}$ zeolites gave the [Pd(II)]−NaY zeolite, and subsequent treatment at 350 °C with pure H_2 (70 mL/min) gave [Pd(0)]−NaY. The absolute palladium content for these catalysts was determined by AAS to be 1 ± 0.2 wt % of Pd. As known from the literature, calcination and reduction of the Pd species at such high temperatures leads to agglomeration and the formation of palladium (oxide) particles. These correspondingly pretreated catalysts can be regarded as the models of lower Pd dispersion.

Analogous to the ion-exchange process used for the above preparations, we prepared the following Pd complexes immobilized in zeolites: $[Pd(OAc)_2]$ and $[Pd(C_3H_5)Cl]_2$ in the zeolite supercage.

Because the diameter of the zeolite channels is limited (for the Y zeolite: $\phi = 7.4$ Å),[14] we performed molecular modeling calculations in order to check whether the complexes can pass through the zeolite window. The results obtained for $[Pd(NH_3)_4]^{2+}$−NaY, $[Pd(OAc)_2]$−NaY, and $[Pd(C_3H_5)Cl]_2$−NaY using the MM2 augmented parameters[15] provided with the CAChe software from Oxford Molecular LTD[16] are reported in Figure 1.

Concerning $[Pd(NH_3)_4]^{2+}$, we did not find any limitation due to its small size and its *pseudo*-spherical geometry which allows it to pass through the zeolite pore in all directions and for all orientations.

Limitations are expected for the$[Pd(OAc)_2]$ and $[Pd(C_3H_5)Cl]_2$ complexes. We found that a perpendicular orientation or an orientation with a minimum angle of 56° for the $[Pd(OAc)_2]$ complex and 42° for the $[Pd(C_3H_5)Cl]_2$ complex, versus the plane defined by the pore, is required for the complex to pass through the pore.

These calculations were supported by the time necessary for sufficient ion exchange. To obtain reasonable amounts of palladium in the zeolite when using the $[Pd(OAc)_2]$ and

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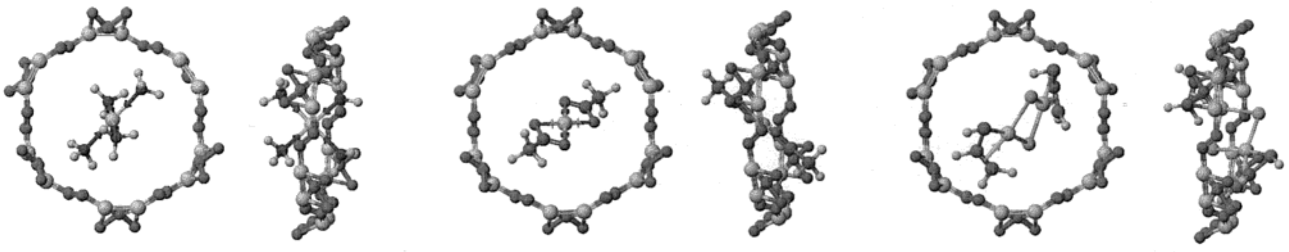
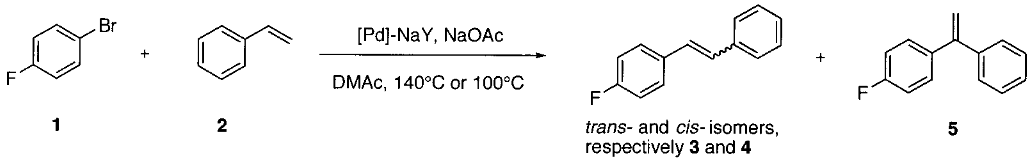


$[Pd(NH_3)_4]^{2+}$-NaY $[Pd(OAc)_2]$-NaY $[Pd(C_3H_5)Cl]_2$-NaY

Figure 1. Molecular modeling of the Pd complexes ($[Pd(NH_3)_4]^{2+}$, $[Pd(OAc)_2]$, $[Pd(C_3H_5)Cl]_2$) in Na-Y zeolite using the CAChe software with extended MM2 molecular force field and molecular mechanics methods.

Scheme 1[a]



[a] Reaction conditions: 10 mmol of 4-bromofluorobenzene **1**, 15 mmol of styrene **2**, 15 mmol of NaOAc, 0.1 mol % of [Pd]−NaY, 8 mL of DMAc, 140 or 100 °C, 20 h.

Table 1. Activity and Selectivity for the Heck Reaction of 4-Bromofluorobenzene with Styrene (Scheme 1) Catalyzed by [Pd]−NaY or, When Available, by the Corresponding Homogeneous Complexes (0.1 mol %)

		product yield [%][a]						
		heterogeneous catalyst			homogeneous catalyst			
catalyst	*T* [°C]	**3**	**4**	**5**	**3**	**4**	**5**	TOF[b]
[Pd(0)]−NaY	140	89.4 [88.2]	0.9	8.2				20
	100	85.1 [78.9]	1.0	7.9				16
[Pd(II)]−NaY	140	90.2 [87.6]	1.0	8.4				80
	100	89.3 [76.2]	0.9	8.1				75
$[Pd(NH_3)_4]^{2+}$−NaY	140	93.0 [89.1]	1.0	8.8	{94.0}	{1.0}	{8.8}	6000
	100	94.5 [89.5]	0.7	6.7	{92.2}	{1.0}	{8.4}	2660
$[Pd(OAc)_2]$−NaY	140	79.2 [68.7]	0.9	7.2	{83.8}	{0.9}	{7.6}	2000
	100	57.6 [39.9]	0.4	3.9	{47.6}	{0.3}	{3.9}	1140
$[Pd(C_3H_5)Cl_2$−NaY	140	86.3 [78.2]	1.0	8.3	{87.1}	{0.9}	{8.4}	2700
	100	74.2	0.5	5.2	{30.9}	{0.2}	{2.1}	1210

[a] GLC yields and [isolated yields] are given and compared to {GLC yields for homogeneous catalysts} ($\Delta_{rel} = \pm10\%$). Reaction time 20 h. [b] Turn-over-frequency calculated at the completion of the reaction (mol of aryl bromide transformed/mol of heterogeneous catalyst)/h using 0.05 mol % of catalyst. Although TOF changes during the reaction, it allows better comparison to other catalysts concerning the activity.

$[Pd(C_3H_5)Cl]_2$ complexes, 3 days were required (giving 0.7% and 0.5% Pd catalyst, respectively). MAS NMR of the Pd complexes in the zeolites have been recorded and confirmed that the immobilized complexes are intact within the zeolite cages. The spectra (^{1}H, ^{13}C) were comparable to the solution NMR spectra obtained for the corresponding free complexes (see Experimental Section).

Catalytic Activity. As a first model reaction, we chose the reaction of 4-bromofluorobenzene with styrene (Scheme 1). This reaction is known to give high yields of the Heck product with homogeneous catalysts, thereby allowing the observation of small changes in activity of the catalysts, particularly when applied to heterogeneous systems.[10]

The conversion and selectivity obtained at two temperatures for the Pd-loaded zeolites (0.1 mol % of Pd/aryl bromide **1**) are reported in Table 1. For the Pd complexes immobilized in NaY zeolite, the results are compared to results obtained with the corresponding Pd complexes in bulk solution (i.e., homogeneous catalysis).

Considering the Pd(0) particles or the ionic Pd species ([Pd(II)] or $[Pd(NH_3)_4]^{2+}$), the results did not show a strong influence of the palladium oxidation state on product yields or product selectivity. Generally the zeolites modified by ionic Pd species gave higher activities. Variations are also observed for the Pd complexes ($[Pd(NH_3)_4]^{2+}$, $[Pd(OAc)_2]$, and $[Pd(C_3H_5)Cl]_2$). The results indicate that the catalytic activity of the Pd-loaded zeolites depends on the nature of the complex. The activity of $[Pd(NH_3)_4]^{2+}$ was higher than that of $[Pd(OAc)_2]$ and $[Pd(C_3H_5)Cl]_2$. This dependence of the activity is probably due to a higher stability of the active Pd species generated from the $[Pd(NH_3)_4]^{2+}$ complex than from the $[Pd(OAc)_2]$ or $[Pd(C_3H_5)Cl]_2$ complexes (ligand effect, see also recovery of the catalysts). These interpretations are supported by the comparison of these results with those of the free Pd complexes in solution (homogeneous catalysts without zeolite). Table 1 illustrates that the Pd complexes immobilized in zeolites have almost the same activity as the free Pd complex. A comparison of the activity of free and immobilized $[Pd(OAc)_2]$ and $[Pd(C_3H_5)Cl]_2$ at 100 °C shows that higher activity for the immobilized complexes is obtained. This is probably due to better stabilization of the active Pd species by the zeolite framework.[12]

For all types of heterogeneous catalysts, Table 1 shows that the activity is less strongly dependent on the temperature of the reaction than expected. Slightly lower yields based on Pd complexes were observed at 100 °C for the catalysts. The 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 recovery of the catalysts).

Kinetic Studies. While we did not observe strong variations for the heterogeneous Heck reaction using standard reaction conditions (Scheme 1: 100 °C or 140 °C, 20 h), clear differences were observed in kinetic experiments. We compared the activity of the [Pd(0)]−, [Pd(II)]−, and $[Pd(NH_3)_4]^{2+}$−NaY catalysts during the reaction between p-$BrFC_6H_4$ (**1**) and the styrene (**2**) under standard reaction conditions (Scheme 1: $T = 140$ °C, 0.05 mol % of [Pd]).

For [Pd(II)]−NaY (Figure 2b) an induction period of ca. 8 min was required before the reaction started. This induction period was not observed for the [Pd(0)]−NaY (Figure 2a). When using [Pd(0)]−NaY the products of the reaction could be detected by GC after 30 s. This result is similar to the observations made with $[Pd(NH_3)_4]^{2+}$−NaY (Figure 2c). With this catalyst, an induction period of ca. 2 min was observed. The curves obtained with [Pd(II)]−NaY or $[Pd(NH_3)_4]^{2+}$−NaY are similar to the ones observed for homogeneous catalysis.[1] The induction period corresponds to the delay required for the reduction of the [Pd(II)] species (catalyst precursor) to the active [Pd(0)]. This reduction is probably caused both by the styrene[17] and by the OH groups present in the zeolite cages.[18] In other experiments,[10a] we observed that the use of HY zeolites instead of NaY as support reduce the induction period from 8 min for the Na form to 4 min for the H form. This corroborates a partial reduction of the [Pd(II)] species by OH groups.

As can be seen from the time axis (in Figure 2), the $[Pd(NH_3)_4]^{2+}$−NaY catalyst was found to be the most active for the reaction. Thus, the Heck reaction of p-$BrFC_6H_4$ with styrene is completed after ca. 20 min using $[Pd(NH_3)_4]^{2+}$−NaY, whereas it required ca. 1450 min when using Pd(II)−NaY and ca. 7200 min when using the Pd(0)−NaY. The selectivity and the activity observed are comparable to those obtained with standard homogeneous catalysts but lower than those obtained with the most recent, most active catalysts.[1,2] The differences in activity of the three catalysts can be rationalized by the different treatment of the catalysts at higher temperature. As reported, such treatments decrease the dispersion of the Pd species entrapped into the zeolite cages.[19] Thus, $[Pd(NH_3)_4]^{2+}$−NaY would present the highest dispersion, since it was not subjected to any thermal treatment after the ion-exchange, in contrast to the [Pd(II)]−NaY or the [Pd(0)]−NaY catalysts. The calcination at 500 °C of $[Pd(NH_3)_4]^{2+}$−NaY to give [Pd(II)]−NaY tends to form aggregated [Pd(II)] species in the zeolite cages. In addition, the reduction temperature influences strongly the size of the [Pd(0)] particles formed in the zeolites. The [Pd(II)] catalyst reduced in situ leads to [Pd(0)] species with higher dispersion, since it is obtained by relatively low-temperature treatment (140 °C). In contrast, the reduced [Pd(0)] catalyst obtained by treatment under an H_2 atmosphere at 350 °C leads to larger palladium particles in the zeolite.[19] 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.

Examination of the Presence of Catalytically Active Species in Homogeneous Bulk Solution ("Leaching"). Leaching of active species from heterogeneous catalysts in solution must be evaluated to identify whether the active centers are solid surfaces or dissolved palladium complexes. As a method, we investigated the residual activity of the supernatant solution after separation of the catalyst. The leaching was studied as followed: the organic phase of a first run was separated from the solid (Pd-modified zeolite). New reagents (p-$BrFC_6H_4$, styrene, and NaOAc) were added to the clear filtrate, and the composition of the reaction mixture was determined by GC. The amount of p-$BrFC_6H_4$ was set to 100%. This homogeneous reaction mixture was treated as a standard catalytic experiment (100 or 140 °C, 20 h). After 20 h, the composition was determined by GC again. The differences observed between the two GC determinations gave qualitative information about the "leaching" (Table 2). While this method did not allow the absolute quantification of the palladium species (active and/or inactive) dissolved, it gave information about the presence or absence of *active* species in bulk solution and the activity of leached species in the heterogeneous Heck reaction. Palladium species dissolved but retained in the zeolite cages cannot be detected by this procedure.

In all cases, the leaching observed cannot explain the overall activity of the catalysts (see also recovery of catalyst). In addition, we never detected Pd in the isolated organic compounds (AAS analysis).

However, small amounts of leaching of palladium were detected. The amount of leaching depended on the temperature of the reaction and on the nature of the Pd species immobilized in the zeolite cages (Table 2). Thus, no leaching was observed for [Pd(0)]−NaY at both temperatures, and a slight leaching (0.6%) was found for [Pd(II)]−NaY at 140 °C. A better stabilization of the [Pd(0)] particles by the zeolite framework at the beginning of the reaction could be an explanation.[12]

For $[Pd(NH_3)_4]^{2+}$, a higher degree of leaching is observed at 140 °C (0.5%) than at 100 °C, at which temperature it was not detected. We did not observe leaching from the immobilized $[Pd(OAc)_2]$ catalyst at either reaction temperature, but we observed a relatively high leaching (9%) from the immobilized $[Pd(C_3H_5)Cl]_2$ catalyst at 140 °C. The leaching was strongly reduced by the use of a lower reaction temperature (i.e., 100 °C). Actually, this observation can be correlated with the relative stability of the complexes under the reaction conditions. Thus, the $[Pd(C_3H_5)Cl]_2$ decomposes quickly at 140 °C ($T_{dec} = 120$ °C),[20] whereas $[Pd(OAc)_2]$ decomposes more slowly ($T_{dec} = 205$ °C)[20] at this temperature. The $[Pd(NH_3)_4]^{2+}$ complex decomposes in two steps: $T_{dec1} = 158$ °C, and $T_{dec2} = 285$ °C,[21] which can explain the slightly better stability of the catalyst obtained at 100 °C.

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

After separation and washing, the heterogeneous catalysts were used several times for the same or similar reactions under the same conditions as for the initial run of the catalyst without any regeneration. The conversion and selectivity are reported in Table 3.

The results depend on the nature of the Pd species entrapped in the zeolite at the beginning of the reaction. Thus, recycled

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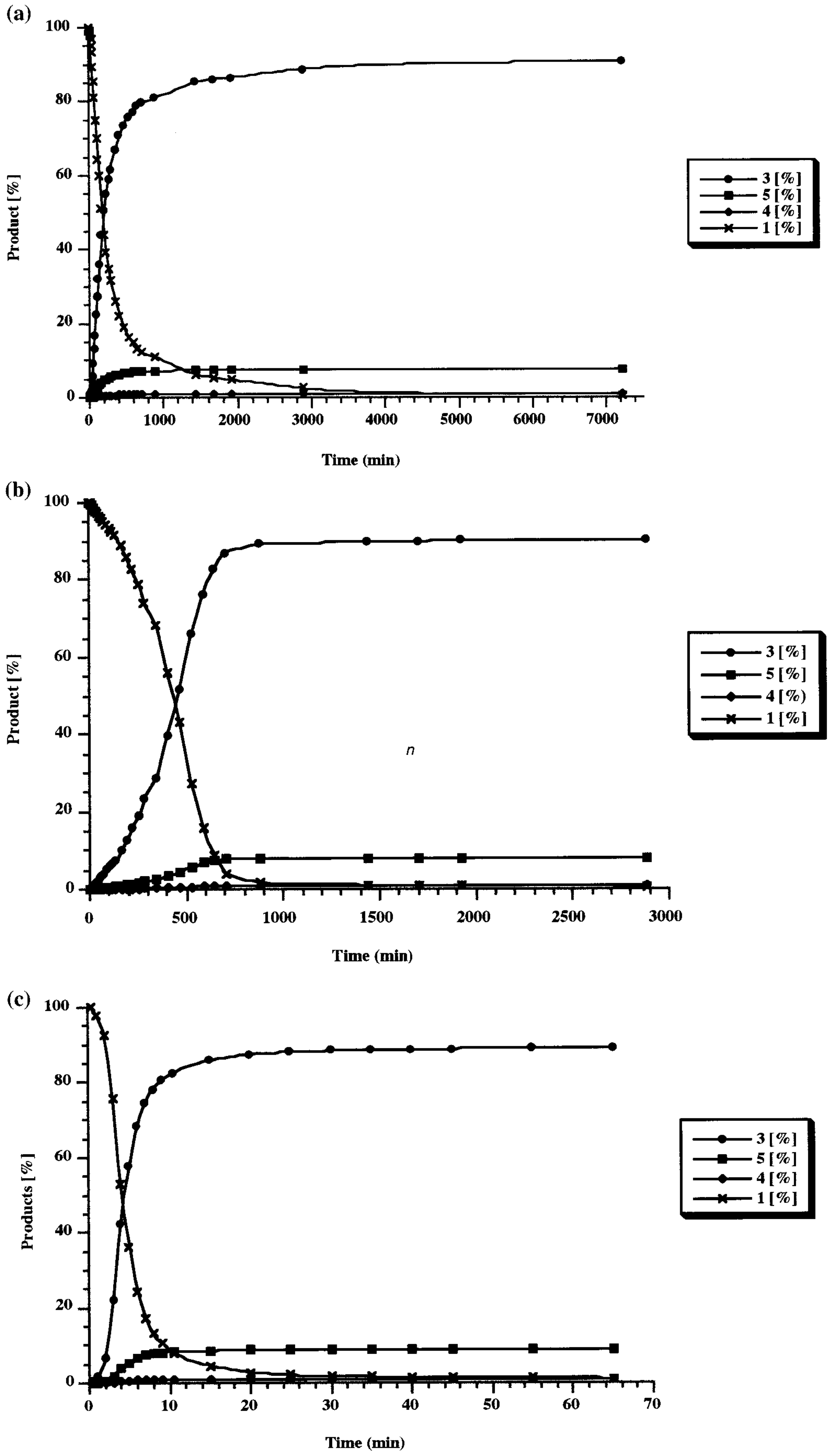

Figure 2. Kinetic investigations: conversion of 4-bromofluorobenzene **1** and product percentage (**3**, **4**, and **5**) obtained with the [Pd(0)]−NaY, [Pd(II)]−NaY, and $[Pd(NH_3)_4]^{2+}$−NaY catalysts, respectively, for the Heck reaction (Scheme 1).

Table 2. Activity and AAS Analysis of the Clear Supernatant

catalysts	*T* [°C] of the first run	activity of the clear supernatant[a]	AAS analysis of the clear supernatant[b]
[Pd(0)]−NaY	140	<1%	<0.5 ppm
	100	<1%	<0.5 ppm
[Pd(II)]−NaY	140	5%	8 ppm
	100	<1%	<0.5 ppm
$[Pd(NH_3)_4]^{2+}$−NaY	140	3%	6 ppm
	100	<1%	<0.5 ppm
$[Pd(OAc)_2]$−NaY	140	<1%	<0.5 ppm
	100	<1%	<0.5 ppm
$[Pd(C_3H_5)Cl_2]$−NaY	140	26%[c])	112 ppm
	100	<1%	<0.5 ppm

[a] The activity of the clear supernatant was measured for the Heck reaction of 4-bromofluorobenzene with styrene (Scheme 1). GLC yields for product **3** [%] resulting from a conversion of the 4-bromofluorobenzene are given ($\Delta_{rel} = \pm 10\%$). Values < 1% are considered to be under the error limit of the analytical method. [b] The AAS analysis was performed on the clear filtrate directly from the organic solution. The detection limit was given to be 0.5 ppm. Values under this limit are regarded as the absence of leaching concerning the analytical method used here. [c] The relatively high activity observed in this case could be due to the leaching of the Pd complex $[Pd(C_3H_5)Cl_2]$ that shows a high activity at that reaction temperature.

Table 3. Heck Reaction of 4-Bromofluorobenzene with Styrene (Scheme 1) Catalyzed by Recovered [Pd]−NaY (0.1 mol %)

catalyst	*T* [°C]	yield of product **3** [%][a] first run	yield of product **3** [%][a] recycled
[Pd(0)]−NaY	140	89.4	86.0
	100	85.1	80.1
[Pd(II)]−NaY	140	90.2	89.2
	100	89.3	88.7
$[Pd(NH_3)_4]^{2+}$−NaY	140	93.0	80.9
	100	94.5	1.0
$[Pd(OAc)_2]$−NaY	140	79.2	81.2
	100	57.6	17.8
$[Pd(C_3H_5)Cl_2$−NaY	140	86.3	72.0
	100	74.2	1.4

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

Table 4. Recovery and Reuse (Catalyst Recycling): Heck Reaction of 4-Bromofluorobenzene with Styrene (Scheme 1) Catalyzed by Recovered [Pd complex]−NaY Used in a First Run at 100 °C (0.1 mol %) Before and After the Regeneration

catalyst	reactivation[b]	yield of product **3** [%][a] first run	yield of product **3** [%][a] recycled
$[Pd(NH_3)_4]^{2+}$−NaY	no	94.5	1.0
	yes		75.2
$[Pd(OAc)_2]$−NaY	no	57.6	17.8
	yes		79.8
$[Pd(C_3H_5)Cl_2$−NaY	no	74.2	1.4
	yes		75.3

[a] GLC yields are given ($\Delta_{rel} = \pm 10\%$). [b] After separation, the solid catalyst was washed with CH_2Cl_2 and dried at room temperature; no additional reactivation or reactivation was made by treating the recycled catalyst for 1 h at 140 °C under the reaction conditions.

Table 5. Yield of **3** [%] in the Heck Reaction of 4-Bromofluorobenzene with Styrene (Scheme 1) Catalyzed by Recovered [Pd(0)]−NaY Used in a First Run at 140 °C (0.1 mol %) with Dependence on the Drying Temperature (24 h) Applied Before Reuse of the Catalyst. In Addition, the Corresponding Weight Loss (Water) Determined by Thermogravimetric Investigation of the Catalyst Is Given

T [°C]	25	60	80	120
3 [%][a]	86.0	50.1	12.9	2.0
weight loss [%]	<1	<1	6	14

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

[Pd(0)]− and recycled [Pd(II)]−NaY show activities comparable to those of the fresh catalysts. The catalysts were used up to five times, and the yields were reduced only slightly (<5% for each reuse).

For the catalysts based on Pd complexes, the situation was different. Table 3 shows that all the complexes used in a first run at 140 °C showed activity that was comparable to the activity observed for the first run. In contrast, the catalysts used in a first run at 100 °C showed a lower activity in these experiments (at 100 °C).

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

The results reported in Table 4 show that the regenerated catalysts showed an activity that was comparable to the high activity observed for the recovered catalysts used in a first run at 140 °C.

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

These results can be compared to results obtained with [Pd(0)]− or [Pd(II)]−NaY, for which we propose that the active species are [Pd(0)] particles entrapped into a zeolite in all situations (100 or 140 °C). We postulate that the active species generated for all catalysts based on Pd complexes in these systems have the same structure at 140 °C. This structure is probably based on [Pd(0)] particles bound into the zeolite cage (the different selectivity of homogeneous catalysts and the Pd/zeolite system to polyaromatic compounds of large molecule diameters are an additional indication for such a reaction inside the zeolite pores, see below).

In other experiments, we evaluated the effect of the catalyst posttreatments after separation from the reaction medium (particularly the drying temperature). After filtration and washing, the catalysts were dried at different temperatures before they were used without any other treatments. The drying temperature played an important role. The results reported in Table 5 for the recycled [Pd(0)]−NaY catalysts showed that the activity decreased dramatically with the drying temperature (the other catalysts gave similar results).

To explain these observations, we measured the loss of volatile compounds (mainly water) by thermogravimetry. The activity of the catalyst decreased as a function of the drying temperature, i.e., the loss of water molecules (Table 5). We postulate that the water molecules present in the zeolite framework act as a “carrier-regulator” for the elimination of the salt from the pores to the bulk solution. The partial elimination of the water molecules from the support probably tends to occlude the pores.

A clearer description of the loss in activity of the catalysts by recycling can be obtained by the reaction of nonactivated aryl bromides and using shorter reaction times. The results of such recovery−reuse experiments are shown in Table 6 for the reaction of bromobenzene with styrene (Scheme 2). With repeated recycling, the mass of the solid (catalyst + residual base + sodium bromide) increased significantly, making handling difficult. Washing the solid with water, in addition to the use of organic solvent, was necessary to remove the base and sodium bromide. The results show that catalyst recycling and reuse is possible, but with clearly decreased activity.

Table 6. Recovery and Reuse (Catalyst Recycling): Yields of *trans*-Stilbene **8** [%] in the Reaction of Bromobenzene and Styrene (Scheme 2, $R^1 = H$, $R^3 = Br$ and $R^2 = Ph$) Catalyzed by $[Pd(NH_3)_4]^{2+}{-}NaY$. The Influence of the Washing Solvent (Dichloromethane or Dichloromethane and Then Water) Is Illustrated

	yields of product **8** [%]^{a,b}		
washing procedure	1st run^{b}	2nd run	3rd run
dichloromethane	87	25	11
dichloromethane + water	87	16	15

^{a} Reaction conditions: 6 h reaction time, 0.1 mol % of Pd, 140 °C, base (sodium acetate) in DMAc. ^{b} GLC yields are given ($\Delta_{rel} = \pm 10\%$). ^{c} Without washing.

Complete conversion can be achieved, however, using longer reaction times (20 h).

Variation of the Educts. (1) Reaction between Aryl Bromides and Olefins. To generalize the results obtained for the heterogeneously catalyzed Heck reaction with the model reaction (Scheme 1), experiments have been conducted using other aryl halides and olefins as substrates and the $[Pd(NH_3)_4]^{2+}{-}NaY$ catalyst (Scheme 2).

The results reported in Table 7 show that the heterogeneous catalyst has a high activity toward the activation of aryl bromides, even for the nonactivated bromoanisole ($R^1 = CH_3O$, $R^3 = Br$). Concerning the variation of the olefins, the electron-poor olefins ($R^2 = Ph$, $^{n}BuO\text{-}CO$) gave better yields than the electron-rich olefins ($R^2 = {}^{n}BuO$) as expected. The activity trend observed for aryl bromides was similar to that observed with homogeneous catalysis and depended on the *para*-substituent and the π-electron density of the olefins.[1,2] In addition to these experiments, kinetic studies have been performed for the reaction of aryl bromides ($R^1 = F$, H, and OCH_3, $R^3 = Br$) with styrene ($R^2 = Ph$) using 0.05 mol % of Pd catalyst. The results showed that $[Pd(NH_3)_4]^{2+}{-}NaY$ is a highly active heterogeneous catalyst for the Heck reaction, including the nonactivated bromobenzene and the "deactivated" 4-bromoanisole. After an initiation period of ca. 2−5 min, complete conversion of the aryl bromides was achieved in 20, 35, and 51 min, respectively, for $R^1 = F$, H, OCH_3.

For a fair comparison of the activity of the Pd/zeolite catalysts to the best heterogeneous catalysts reported in the literature very recently, the Heck reaction of bromobenzene with styrene or methyl acrylate is the most suitable and important. It can be concluded from Table 8 that the activity of the $[Pd(NH_3)_4]^{2+}{-}NaY$-zeolite system reported here exceeds that of the other catalysts by at least 1 order of magnitude (TOF, reaction rate). In addition, the necessary reaction temperature is lower.

(2) Activation of Aryl Chlorides. Another important issue concerning the heterogeneous Heck reaction is the possibility to activate the economically more interesting aryl chlorides. To examine this possibility, we studied the reaction between 4-chloroacetophenone ($R^1 = CH_3CO$, $R^3 = Cl$, Scheme 2) and styrene ($R^2 = Ph$) using $[Pd(NH_3)_4]^{2+}{-}NaY$ as heterogeneous catalyst.

As expected, the results reported in Table 9 show that the activation of aryl chlorides required a higher temperature than did activation of the bromo derivatives. This result parallels the halogen−carbon bond energy, which was calculated for bromoacetophenone (ca. 80.5 kcal/mol)[22] and chloroacetophenone (ca. 96 kcal/mol).[22] However, one should also consider that the Pd−Cl bond is stronger in the resulting Pd complex, and this stronger bond makes the thermodynamics for activation of aryl chlorides more favorable. As already mentioned in the literature, an interesting salt effect was observed with $n\text{-}Bu_4NBr$.[23] Addition of this salt gave increased activity for this reaction, but this increased activity was accompanied by a dehalogenation reaction leading to the formation of acetophenone in 8.3% yield.

(3) Selectivity of the Heterogeneously Catalyzed Heck Reaction. In addition to the experiments described, we were interested in studies concerning the selectivity of the Heck reaction using cyclic olefins (Scheme 3).

While this area was extensively studied using homogeneous catalysts,[24] the isomerization of the product and the formation of polyaryl compounds by successive Heck coupling reactions remains an important problem.

As a model reaction, we chose the coupling of 4-bromoacetophenone with cyclohexene (Scheme 3). This reaction is known to be difficult. Low reactivity of this olefin is generally observed in the Heck reaction, but this olefin provides the advantage of limiting the number of possible product isomers. We compared reactions containing the $[Pd(NH_3)_4]^{2+}{-}NaY$ heterogeneous catalyst with those containing a standard homogeneous catalyst $[Pd(OAc)_2/PPh_3]$.

The results reported in Table 10 show that we obtained almost the same selectivity (respectively **13:14:15** ≈ 1:15:84 in DMAc) using a heterogeneous catalyst as with homogeneous systems and that the product **15** is formed as the major isomer. As found by molecular modeling calculations,[25] such a distribution would correspond to the formation of the thermodynamically most stable isomer. In addition, we found that replacing DMAc by DMF as solvent would disfavor the formation of acetophenone **16**, one of the main side products of the reaction. While conversion of the aryl bromides is low compared to that of homogeneous systems (possibly due to the diffusion control), the heterogeneous catalysts are never formed polyaromatic compounds, which represent 10−12% of the products formed with homogeneous systems. This observation can be rationalized by the similar sizes of zeolite pores, and the polyaromatic compounds and can be interpreted as an interesting example of product form selectivity of zeolite-based catalysts.

Conclusions

[Pd]−NaY zeolites exhibit a high activity toward the Heck reaction of aryl bromides with olefins, under standard reaction conditions. Small amounts of palladium (0.1 mol %) are required to perform the 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 ($R^2 = Ph$, $^{n}BuO{-}CO$) react nearly quantitatively. The catalysts can be easily separated from the reaction mixture (filtration) and reused after washing. Depending on the reaction temperature, some catalysts were deactivated during the extraction. However, active species could be regenerated by a simple procedure. Except for

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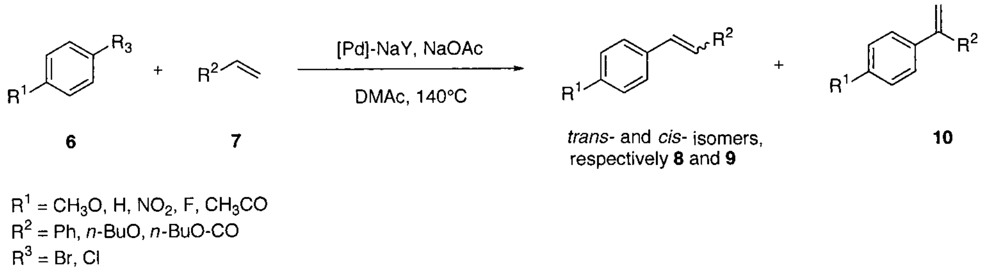
[25] CAChe version 4.1.1 for PowerMacintosh from Oxford Molecular Ltd. was used for the molecular modeling.

Scheme 2[a]



[a] Reaction conditions: 10 mmol of aryl halide **6**, 15 mmol of olefin **7**, 15 mmol of NaOAc, 0.1 mol % of [Pd]−NaY, 8 mL of DMAc, 140 °C, 20 h.

Table 7. Heck Reaction of Various Aryl Bromides with Different Alkenes (Scheme 2, R^3 = Br) Catalyzed by $[Pd(NH_3)_4]^{2+}$-NaY at 140°C (0.1mol % Pd)

		product yield [%][a]		
R^1	R^2	**8**	**9**	**10**
CH_3O	Ph	81.2 [75.8]	9.5	
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_3CO	Ph	93.7 [79.6]	1.1	4.9
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 ($\Delta_{rel} = \pm 10\%$).

one catalyst ($[Pd(C_3H_5)Cl]_2$−NaY used at 140 °C), no substantial leaching was observed.

The kinetics performed with $[Pd(NH_3)_4]^{2+}$−NaY showed that the heterogeneous catalysts have an activity comparable to that of the homogeneous catalysts. Complete conversion of nonactivated aryl bromides was achieved after ca. 30 min. This represents the most active heterogeneous catalyst for the activation of aryl bromides reported up to now. We also 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. In the Heck reaction with cyclic olefins, the zeolite obviously controls the selectivity of the reaction by the well established "product form selectivity". No polyaromatic side products were formed.

On the other hand the turnover numbers are one or several orders of magnitude lower than those of the best homogeneous catalytic systems (reviewed in ref 1g). Nevertheless, the catalysts reported here can be regarded as an important step toward simple systems with the potential for commercial application of heterogeneous catalysts in CC coupling reactions. The possibility of carrying out the reactions without exclusion of air and moisture and using nondried solvents are of particular interest for practical applications. In addition, separation of the catalyst by filtration is easy and possible within a short time for the zeolites (large grain size) in comparison to various silicas.

Whereas the reaction mechanism of the homogeneously catalyzed Heck reaction is today generally accepted,[1] the mechanism of the heterogeneously catalyzed Heck reaction remains unclear. Our experiments indicate that Pd(0) species are the active species as they are for the homogeneous systems. The results observed are consistent with an oxidative addition of the aryl bromide to the Pd(0) center. In addition, the identical product distributions in the homogeneous and heterogeneous reactions suggest a similar reaction mechanism for both. At this stage, we propose that a homogeneous mechanism takes place in the zeolite cage for the heterogeneous Heck reaction using Pd complexes entrapped in zeolites. The active palladium species could be complexes formed in situ by decomposition of the entrapped Pd complexes. These complexes may coexist with adsorbed entities by a dissolution−adsorption equilibrium of Pd(0/II) species but are retained in the zeolite cages. Current investigations focus on kinetic and mechanistic aspects.

Experimental Section

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 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. 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 an Ar atmosphere.

Solution NMR spectra of the organic products were recorded with a Bruker AM 400 spectrometer (^1H NMR were referenced to the residual protio solvent: $CDCl_3$, d = 7.25 ppm. ^{13}C NMR were referenced to the C-signal of the deutero solvent: $CDCl_3$, d = 77 ppm).

Solid-state ^1H and ^{13}C 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 ^1H and ^{13}C MAS NMR spectra, approximately 300 mg of the sample was packed into 4 mm ZrO_2 Bruker rotors with Kel-F caps. ^1H 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. ^1H MAS NMR spectra were recorded at a sample spinning speed of 15 kHz. The ^{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.

Gas chromatography was performed on a 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.

Preparation of the Catalysts. (1) Procedure for the Preparation of $[Pd(NH_3)_4]$−NaY. A 0.1 M ammonia solution of $[Pd(NH_3)_4]Cl_2$—prepared from $PdCl_2$ and a commercial ammoniac solution—(0.95 mL/g zeolite, corresponding approximately to 1% Pd in the final catalyst) was added dropwise to a suspension of the zeolite Na-Y in bi-distilled water (100 mL/g of zeolite). The mixture was stirred for 24 h at room temperature 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 AAS gave 1.0 ± 0.2 wt % of Pd.

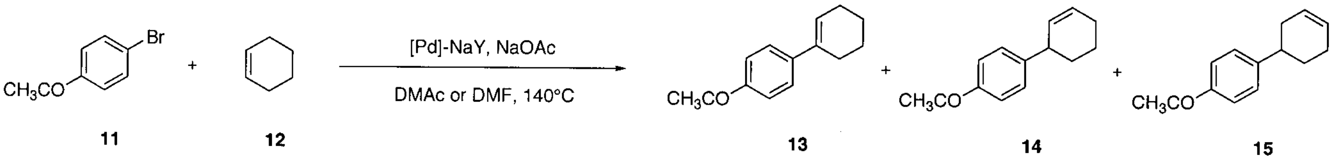
(2) Procedure for the Preparation of [Pd(II)]−NaY. The Pd(II)−NaY was obtained by calcination of the entrapped $[Pd(NH_3)_4]$−NaY in a U-reactor under a pure oxygen flow (180 mL/min) using a heating rate of 2 K/min from room temperature to 500 °C. The temperature

Table 8. Comparison of the Activity and Reaction Conditions of Heterogeneous Catalysts in the Heck Reaction of Bromobenzene with Styrene (Scheme 2, $R^1 = H$, $R^3 = Br$ and $R^2 = Ph$) and Methyl Acrylate (Scheme 2, $R^2 = CH^3O{-}CO$) Published in the Literature Very Recently

catalyst	catalyst concentration [mol %][a])	reaction temp [°C]	reaction time [h]	yield **8−10** [%] (all coupling products)	TON[b]	TOF[c] [h^{-1}]	reference
Pd/C[d]	>1	160	12	<20	≤20	2	Zhao et al. [6o]
Pd/mesoporous silica	0.1	170	48	39	390	8	Mehnert et al.[7b]
polymer- supported Pd carbenes	0.02	150	60	75	3750	63	Schwartz et al.[5j]
$[Pd(NH_3)_4]^{2+}$/Na-Y	0.05	140/100	0.5	96	1920	3840	this paper

[a] mol of Pd/mol of bromobenzene. [b] [mol of coupling product (all isomers)]/(mol of Pd). [c] TON/reaction time in hours. [d] Reaction of bromobenzene and methyl acrylate. High selectivity (up to 80%) to undesired benzene (dehalogeneation).

Scheme 3[a]



[a] Reaction conditions: 10 mmol of 4-bromoacetophenone **11**, 15 mmol of cyclohexene **12**, 15 mmol of NaOAc, 0.1 mol % of [Pd]−NaY, 8 mL of DMAc or DMF, 140 °C, 20 h.

Table 9. Heck Reaction of an Aryl Chloride with Styrene (Scheme 2, $R^1 = CH'_3CO$, $R^2 = Ph$, $R^3 = Cl$) Catalyzed by $[Pd(NH_3)_4]^{2+}$−NaY at 140 or 170 °C (0.1 mol % of Pd)

T [°C]	cocatalyst[a]	product yield [%][a] **8**	**9**	**10**
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] *t*-Bu_4NBr. [b] GLC yields and [isolated yields] are given ($\Delta_{rel} = \pm 10\%$).

Table 10. Heck Reaction of Aryl Bromides with Cyclic Alkenes (Scheme 3) Catalyzed by $[Pd(NH_3)_4]$−NaY at 140 °C (0.1 mol % of Pd)

solvent	product yield [%][a] **13**	**14**	**15**	**16**[c]	conversion of **11** [%][b]
DMAc	0.1 (0.7)	2.1 (15.1)	11.7 (84.2)	15.0	29.1
	3.1 (4.6)	**13.1 (18.9)**	**54.1 (78.2)**	**7.0**	**86**
DMF	0.1 (0.2)	8.6 (19.0)	36.5 (80.7)	0.8	46.4
	2.8 (3.5)	**10.0 (12.4)**	**68.1 (84.1)**	**1.1**	**94**

[a] For heterogeneous (plain text) and **homogeneous (bold text)** catalysts, GLC yields and (relative selectivity for Heck products) are given ($\Delta_{rel} = \pm 10\%$). [b] Determined by GLC ($\Delta_{rel} = \pm 10\%$). [c] Acetophenone is the major side product in the reaction.

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)−NaY as a tobacco-colored powder. The Pd(II)-loaded zeolite was then stored under an Ar atmosphere to prevent hydration. The AAS gave a 1.0 ± 0.2 wt % of Pd.

(3) Procedure for the Preparation of [Pd(0)]−NaY. The Pd(0)−NaY was obtained by reduction of Pd(II)−NaY in a U-reactor under a pure hydrogen flow (70 mL/min) using a heating rate of 8 K/min from room temperature to 350 °C. The temperature was maintained at 350 °C for 15 min, and the reactor was cooled to room temperature under a flow of argon to give Pd(0)−NaY as a black powder. The Pd(0)-loaded zeolite was then stored under an Ar atmosphere to prevent reoxidation. The AAS gave a 1.0 ± 0.2 wt % of Pd.

(4) Procedure for the Preparation of $[Pd(OAc)_2]$−NaY. A solution of the $Pd(OAc)_2$ (110.2 mg, 0.47 mmol, corresponding approximately to 1% Pd in the final catalyst) in THF was added dropwise to a suspension of the zeolite Na-Y (4.95 g) in THF (20 mL/g of zeolite). The mixture was stirred for 3 days at room temperature, and the $[Pd(OAc)_2]$-loaded zeolite was filtered off and washed with THF until no trace of non-immobilized complex was detected in the filtrate. Then the zeolite was allowed to dry at room temperature to give the entrapped $[Pd(OAc)_2]$ zeolite as a slightly brown material. The AAS gave a 0.7 ± 0.2 wt % of Pd.

MAS NMR: ^1H NMR, ppm 2.10 (CH_3CO).

MAS NMR: ^{13}C NMR, ppm 186,84 (CH_3CO); 23.04 (CH_3CO).

(5) Procedure for the Preparation of $[Pd(C_3H_5)Cl]_2$−NaY. A solution of $[Pd(C_3H_5)Cl]_2$ (88.4 mg, 0.47 mmol, corresponding approximately to 1% Pd in the final catalyst) in THF was added dropwise to a suspension of the zeolite Na-Y (4.95 g) in THF (20 mL/g of zeolite). The mixture was stirred for 3 days at room temperature, and the $[Pd(C_3H_5)Cl]_2$ loaded zeolite was filtered off and washed with THF until no trace of non-immobilized complex was detected in the filtrate. Then the zeolite was allowed to dry at room temperature to give the entrapped $[Pd(C_3H_5)Cl]_2$ zeolite as a yellow material. The AAS gave a 0.5 ± 0.1 wt % of Pd.

MAS NMR: ^1H NMR, ppm 2.14 ($CH^1H^2CHCH^1H^2$); 4.03 ($CH^1H^2CHCH^1H^2$); 7.15 ($CH^1H^2CHCH^1H^2$).

MAS NMR: ^{13}C NMR, ppm 107.15 (CH_2CHCH_2); 69.07 (CH_2CHCH_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 GC signals), and GC yields are in parentheses (= relative area of GC 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.

(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 mass of catalysts depending of the palladium concentration) was introduced in a pressure tube under argon. Then 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 preheated oil bath at 100 or 140 °C for 20 h with vigorous stirring and then cooled to room temperature before the reaction mixture was analyzed by GC.

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 room temperature.

(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 homogenized. A GC analysis of the composition of the mixture was made before the reactor was placed in a preheated oil bath at 100 or 140 °C for 20 h with vigorous stirring. After the reaction, the reactor was cooled to room temperature and a second GC analysis was performed. The comparison between the two GC analyses gave a qualitative measure for the presence of active species in homogeneous/bulk solution.

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Supporting Information Available: Additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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