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Pd–Zeolites as Heterogeneous Catalysts in Heck Chemistry

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Heck reactions were performed with 4-bromoacetophenone and *n*-butyl acrylate, yielding the *trans*-arylated acrylate ester with high selectivity. Pd–zeolite catalysts were compared with supported Pd metal catalysts. In order to obtain an active and heterogeneous catalyst, the preformed or *in situ*-formed catalytically active Pd^0 species and the Pd^{II} intermediates must be sufficiently stabilized on the zeolites against leaching and against aggregation to inactive Pd black precipitates. The different states of Pd in the zeolites, i.e., $Pd(NH_3)_4^{2+}$, lattice-coordinated Pd^{2+} ions, PdO particles, and Pd^0 metal particles of different sizes, were studied by a combination of diffuse reflectance UV–vis, XRD, SEM, and TEM before, during, and after catalytic reactions. The heterogeneous nature of the catalysis largely depends on the catalyst pretreatment and on the solvent and base used. With tributylamine as the base and in toluene, the Heck olefinations with $Pd(NH_3)_4^{2+}$–zeolites (0.4 wt% Pd; mordenite, Y, ZSM-5) and Pd^0–mordenite (0.4 and 4 wt% Pd) are truly heterogeneous. Pd leaching from the zeolites, as evaluated in a very strict filtrate activity test, is clearly related to the presence of oxidized Pd^{II} in an all-oxygen environment, i.e., ionic Pd^{2+} or PdO. Supported Pd catalysts (Pd/C and Pd/SiO_2) give rise to Pd leaching as well. The heterogeneous reactions with the zeolites can be accelerated by the addition of a quaternary ammonium salt promoter. In addition, the heterogeneous Heck catalysts can be applied in a continuous reactor. © 2002 Elsevier Science (USA)

Key Words: **Heck reaction; Pd–zeolite; palladium species; heterogeneous catalysis; zeolites; cinnamates; batch and continuous reactor.**

INTRODUCTION

The Pd-catalyzed arylation or vinylation of olefins, universally referred to as the "Heck reaction," has received increasing attention in the last decade, as it is a selective method to form new C–C bonds in a single operational step (1, 2). The reaction is appealing because of its tolerance of nearly any solvent and functional group on the substrates, its high selectivity, and its moderate toxicity (3, 4). It constitutes a powerful and versatile method for the synthesis of polyfunctional compounds, e.g., dienes, cinnamic esters, and other variously substituted olefinic compounds, which are primarily applied as dyes, UV absorbers, and intermediates for pharmaceuticals, agrochemicals, and fragrances (5, 6). The classical Heck mechanism comprises four steps, starting with the oxidative addition of an aryl or vinyl halide on the coordinatively unsaturated 14-electron-Pd^0 species (step **1**). After coordination and insertion of the olefin to form an organoPd^{II} compound (step **2**), the Heck product is released by a reversible β-H elimination (step **3**). Steps **2** and **3** occur through a square planar transition state and are decisive for the stereo- and regioselectivity of the inter- and intramolecular Heck reactions. In the last step (step **4**) the Pd^0 catalyst is regenerated from the H–Pd–halide intermediate by neutralization of the hydrogen halide by a base; hence, regeneration of the catalyst requires a stoichiometric amount of base.

Currently, the Heck reaction is a landmark in small-scale organic preparations (7). However, a suitable, versatile, and reusable heterogeneous catalyst might increase the applicability of Heck chemistry in commercial processes. Among the various work on heterogeneous Heck catalysis (4, 5, 8–28), several approaches deserve particular attention. A mesoporous SiO_2 with highly dispersed Pd (Pd–TMS11) was used by Ying and co-workers as heterogeneous catalyst in the Heck reaction of *n*-butyl acrylate with a bromoaromatic compound (21, 22). The Pd was deposited in the porous framework by adsorption of a neutral Pd–allyl precursor. Good activity (TON up to 5000 for an activated arylbromide) was reported without leaching of Pd, but recycling of the Pd–TMS11 catalyst was hampered by Pd metal agglomeration, partial structural damage to the support, and deactivation by coke deposition. Djakovitch and co-workers prepared even much more active Heck catalysts by entrapping Pd^0 and Pd^{II} compounds in the micropores of FAU and MOR zeolites (23–26). With $Pd(NH_3)_4^{2+}$ encapsulated in zeolite Y as catalyst, a nonactivated arylbromide is completely converted in a few minutes. They propose that dissolved active Pd^0 species catalyze the Heck reaction in the channels or cages by a homogeneous mechanism. The dissolved Pd species would be retained inside the zeolite structure by dissolution–adsorption equilibria of Pd^0 and Pd^{II}. A similar dissolution and readsorption mechanism is described by Arai and co-workers (27, 28). As

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the vinylation of iodobenzene with methyl acrylate in the presence of Na_2CO_3/NEt_3 starts, significant amounts of Pd leach out from the commercially available Pd/C into NMP (N-methylpyrrolidone) and the reaction is mainly catalyzed by the Pd species in the liquid phase. However, after the reaction is completed almost all the dissolved Pd species can readsorb onto the surface of the carbon support. Of course, such a pseudoheterogeneous system would fail in a continuous reactor.

The main goal of this study is to evaluate the suitability of Pd zeolites as heterogeneous Heck catalysts. In the context of Heck chemistry, a catalyst is heterogeneous if the reaction is catalyzed by Pd species immobilized in or on a support, and this during the whole course of the reaction. As a model, catalysis is studied in the Heck reaction between *n*-butyl acrylate and an activated arylbromide, namely 4-bromoacetophenone. In this reaction, the influence of the reaction conditions and the support type on the heterogeneity of the Pd-catalyzed Heck reactions is determined. Moreover, the relation between the Pd speciation resulting from different pretreatments and the heterogeneity and activity of the Pd catalysts is established in detail. Special attention is devoted to a detailed knowledge of the "exact" nature (homogeneous or heterogeneous) of the catalysis. An additional important aim is to accelerate the reaction by addition of suitable promoters. Finally, the use of a heterogeneous Heck catalyst in a continuous reactor is evaluated.

EXPERIMENTAL

Catalyst Preparation and Pretreatment

Table 1 gives data on the commercial catalysts and the zeolite supports, viz. their origin, crystal size, Si/Al ratio, and counter ion. Unless indicated otherwise, the mordenite sample with Si/Al = 5.7 was employed. Before use, H^+– and NH_4^+–zeolites were converted to the Na^+ form. To suspensions of H^+–zeolites, a dilute ammonia solution was added dropwise until neutral pH. Next, the NH_4^+–zeolites were suspended in water containing a fivefold excess of NaCl with regard to the CEC. After stirring and refluxing these suspensions for 6 h, the solids were isolated by filtration and washed with a large amount of water. This procedure was repeated to obtain Na^+–zeolites as starting materials. The Na^+–zeolites are ion exchanged with an aqueous solution of $Pd(NH_3)_4Cl_2$. The liquid/solid ratio in the suspensions is kept at 100 ml per zeolite. For 4 wt% Pd–zeolites, the suspension of the zeolite in the $Pd(NH_3)_4Cl_2$ solution is thoroughly stirred for 20 h. In the preparation of 0.4 wt% Pd–zeolites, a competitive exchange procedure, as reported by Le Page *et al.*, is followed in order to obtain an adequate distribution (29); in this competitive ion exchange a 25-fold molar excess of NaCl with regard to Pd is added and stirring is continued for 100 h. After filtering, washing, drying, and calcination under O_2 at 500°C (1°C/min, 8 h at 500°C), Pd^{II}–zeolites are obtained. Pd^0–zeolites are prepared by a pretreatment under N_2 at high temperature (12 h, 500°C) or by a H_2 reduction at room temperature of the oxidized Pd^{II}–zeolites. SiO_2 (Silica Gel 60 from Fluka) is impregnated with 4 wt% Pd using the acetate salt and following the incipient wetness technique (29). For all materials, metal loadings are expressed as weight percent metal per mass of dry catalyst.

The Pd catalysts are characterized by AAS (atomic absorption spectroscopy; Varian, SpectrAA-20 Plus), X-ray diffraction (Siemens D5000 diffractometer, filtered CuK_α radiation, $\lambda = 0.154187$ nm, operating at 40 kV and 50 mA), UV–vis diffuse reflectance spectroscopy (Cary 5), scanning electron microscopy (Philips XL30 FEG), and transmission electron microscopy (Philips CM20).

Catalytic Heck Reaction in a Batch Reactor and in a Continuous Tube Reactor

The Pd-catalyzed Heck reactions are performed in a well-stirred glass batch reactor (8 ml, 700 rpm). The reaction

TABLE 1

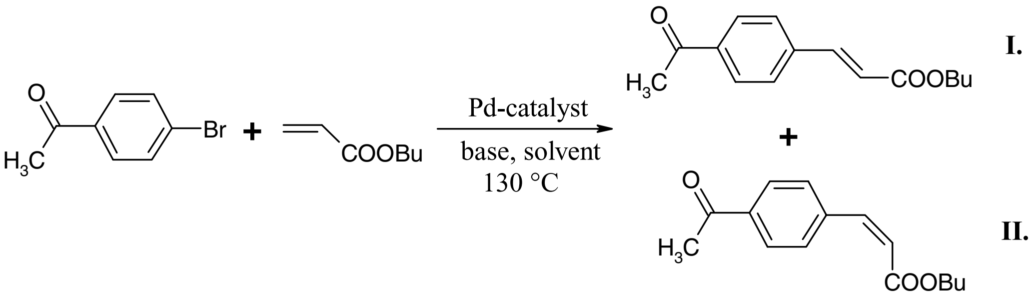
Specification of the Counter Ion, the Source, the Si/Al Ratio, and the Particle Dimensions of the Used Catalysts and Zeolite Supports

Support/catalyst	Counter ion	Origin	Overall Si/Al ratio	Crystal size (μm)[a]
Mordenite	Na^+	Norton Zeolon 100	5.7	1.5–3.5
Mordenite	H^+	Zeocat ZM510	6.47 (11[b])	1–2
Mordenite	NH_4^+	PQ Zeolites BV, CBV 30A	17.5	ND[c]
ZSM-5	Na^+	Zeocat PZ-2/40	18.6	0.2
Y	Na^+	Zeocat	2.71	2–3
Pd/C (5 wt% Pd)	—	Johnson Matthey	—	
SiO_2 (Kieselgel 60)	—	Fluka	—	

[a] Based on SEM results.

[b] Bulk Si/Al ratio.

[c] ND, Not determined.



SCHEME 1. Heck reaction of 4-bromoacetophenone with *n*-butyl acrylate to *n*-butyl *trans*-3-(4-acetylphenyl)acrylate (**I**) and *n*-butyl *cis*-3-(4-acetylphenyl)acrylate (**II**).

mixture consists of 3 mmol aromatic compound, 4.5 mmol vinylating agent, 3.3 mmol base (amine or sodium acetate), and a Pd catalyst (0.125 mol% Pd based on the starting aryl compound) in 3 ml solvent (N,N-dimethylacetamide, DMA, or toluene). The glass flasks are closed with a cap and are immersed in an oil bath with a temperature of 130°C (±1°C). One-microliter samples are withdrawn through the septum and immediately analyzed on a HP 5890A GC (equipped with a 10-m HP-1 Methyl Silicone Gum column and a FID detector). GC-MS (GC 8000 of Fisons Instruments, equipped with a 30-m BPX5 SGE column and a mass-spectrometer MD 800) and liquid ^{1}H and ^{13}C NMR (Bruker AMX 300), after product workup, are applied for a detailed product identification.

Spectral data for *n*-butyl *trans*-3-(4-acetylphenyl) acrylate (Scheme 1, **I**): ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 7.97$ (d, 2H, Aryl, $J = 8.8$ Hz), 7.69 (d, 1H, –Ph–CH=C*H*–, $J = 16.2$ Hz), 7.61 (d, 2H, Aryl, $J = 8.8$ Hz), 6.52 (d, 1H, –Ph–C*H*=CH–, $J = 16.2$ Hz), 4.23 (t, 2H, CH$_2$), 2.61 (s, 3H, CH_3–CO–Ph–), 1.69 (quintet, 2H, CH$_2$), 1.44 (sextet, 2H, CH$_2$), 0.97 (t, 3H, CH$_3$). MS: 246 (M$^+$), 231 (M$^+$ – CH$_3$), 190 (M$^+$ – C$_4$H$_8$), 175 (OC$^+$–C$_6$H$_4$–CH=CH–COOH), 173 (M$^+$ – OBu), 147 (C$_6$H$_4^+$–CH=CH–COOH), 131 (C$_6$H$_5$–CH=CH–CO$^+$), 115 (CH$_2^+$–COOBu), 102 (C$_6$H$_4$–CH=CH$^+$), 91 (C$_7$H$_7^+$), 76 (C$_6$H$_4^+$), 43 (CH$_3$–CO$^+$).

A tube reactor with a diameter of 0.008 m and a length of 0.20 m was used for a continuous Heck experiment. At the inlet, a zone of 0.08 m is filled with glass beads (0.002-m diameter), in which the reagents are heated to the reaction temperature of 130°C. The catalyst bed (0.115 m) is separated from these beads by a glass wool plug and contains 3.42 g of Pd(NH$_3$)$_4^{2+}$–Y particles (0.4 wt% Pd, 500–800 μm). The feed consists of 66.6 mmol 4-bromoacetophenone (13.267 g), 100 mmol *n*-butylacrylate (12.8 g), 86.7 mmol tributylamine (16.033 g), and 200 ml toluene and is pumped (Bioblock Scientific, Eldex Laboratories, Inc.) upstream over the tube reactor at a flow of 1.75 ml/h. The effluent composition is analyzed on the GC described above, and the Pd content of the effluent was determined by ICP–OES (optical emission spectroscopy).

Heterogeneity Test

The heterogeneous nature of the catalysis and the catalysts' stability are examined by a thorough study of Pd leaching to the solution. An attempt was made to discriminate between catalytically active and nonactive Pd species in the solution. The catalytically *active* Pd species are detected by a filtration test (30): at 5–25% conversion of the aryl compound the catalyst is separated from the reaction suspension. After centrifugation (2000 rpm) and filtration (0.2 μm) of the hot suspension, reaction progress is further monitored in the filtrate and in the catalyst suspension. In a complementary approach, AAS and ICP–OES elemental analysis are used to detect the total Pd in the reaction filtrates, including catalytically *inactive* Pd species. It is crucial to perform both analyses, in order to gain insight into the true nature of the catalyst (homogeneous or heterogeneous) and into the nature of the catalytically active Pd species.

RESULTS AND DISCUSSION

Catalyst Characterization

The effect of the different pretreatments on the Pd catalysts can be followed by UV–vis diffuse reflectance spectroscopy and by X-ray diffraction, which give information on the oxidation and coordination state of Pd (31–34). The results are summarized in Table 2. Additionally, the presence of oxide or metal particles was checked by TEM.

After ion exchanging the Na$^+$–zeolites with 0.4 or 4 wt% Pd(NH$_3$)$_4$Cl$_2$, the white color of the starting materials is maintained. The presence of Pd(NH$_3$)$_4^{2+}$ cations in the different zeolites is confirmed by an absorption at approximately 299 nm in the DRS spectra, which agrees well with earlier literature data (32).

The nature of the Pd$^{\text{II}}$ species obtained by calcination of Pd(NH$_3$)$_4^{2+}$–mordenite under O$_2$ largely depends on the Pd concentration. The 0.4 wt% Pd–mordenite turns pink upon calcination; it contains isolated Pd^{2+} cations coordinated to lattice sites, as indicated by an absorption at 477 nm in the

TABLE 2

Characterization of Pd Catalysts: Pd Content, Preparation and Pretreatment, the Prevailing Pd Species, the Color, and the Results of X-Ray Diffraction and UV–Vis Diffuse Reflectance Spectroscopy

Catalyst	Pd content[a]	Preparation, pretreatment[b]	Pd species	Color	XRD[c]	UV–vis DRS (nm)
$Pd(NH_3)_4^{2+}$–MOR	0.4	CIE	$Pd(NH_3)_4^{2+}$	White	MOR	299 (sh 230)
$Pd(NH_3)_4^{2+}$–Y	0.4	CIE	$Pd(NH_3)_4^{2+}$	White	Y	299 (weak 223)
$Pd(NH_3)_4^{2+}$–ZSM-5	0.4	CIE	$Pd(NH_3)_4^{2+}$	White	ZSM-5	299
$Pd(NH_3)_4^{2+}$–MOR	4	IE	$Pd(NH_3)_4^{2+}$	White	MOR	299 (sh 230)
Pd^{2+}–MOR	0.4	CIE, calc	Pd^{2+}	Pink	MOR	477
PdO–MOR	4	IE, calc	PdO	Tobacco brown	MOR + $2\theta = 34^\circ$ [d]	Broad
Pd^0–MOR	0.4	CIE, calc, red (H_2, RT)	Pd^0	Bright grey	MOR	Broad
Pd^0–MOR	4	IE, calc, red (N_2, 500°C)	Pd^0	Dark grey	MOR + $2\theta = 40^\circ$ + $2\theta = 47^\circ$ [e]	Broad
Pd^0–MOR	4	IE, calc, red (H_2, RT)	Pd^0	Black	MOR + $2\theta = 40^\circ$ + $2\theta = 47^\circ$ [e]	Broad
Commercial Pd/C	5	—	Pd^0	Black	$2\theta = 40^\circ$ + $2\theta = 47^\circ$ [e]	Broad
Pd/SiO_2	4	Impregnation	Pd^0	Black	$2\theta = 40^\circ$ [e]	Broad

[a] Weight percent, verified by AAS.

[b] CIE, Competitive ion exchange; IE, ion exchange; calc, calcination; red, reduction.

[c] Zeolite phase + other reflections.

[d] $2\theta = 34^\circ$, plane 101 of PdO.

[e] $2\theta = 40^\circ$, plane 111 of Pd^0; $2\theta = 47^\circ$, plane 200 of Pd^0.

DRS spectrum (31–33). At higher Pd loading, not all the ionic Pd^{2+} can be accommodated at lattice sites, and as a result large tobacco-brown PdO clusters are formed on the external surface of the 4 wt% Pd–mordenite crystals (35). This is apparent from the $2\theta = 34^\circ$ signal (plane 101) in the XRD diffractogram (Fig. 1d) and from TEM (Fig. 2a). By rotating the mordenite sample during the TEM experiment, the PdO clusters appear one by one on the outer surface of the mordenite crystallites.

Reduction of these calcined Pd–mordenites by H_2 at room temperature results in a light grey and a black color for 0.4 and 4 wt% Pd^0–mordenite, respectively. This points to the formation of Pd^0 clusters, which is confirmed by the XRD diffractogram of 4 wt% Pd^0–mordenite (H_2) of Fig. 1f, with Pd^0 diffraction lines at $2\theta = 40^\circ$ (plane 111) and 47° (plane 200). Although no XRD lines are perceived for 0.4 wt% Pd^0–mordenite (Fig. 1e), Pd^0 clusters are observed in TEM analysis.

However, Pd^0 clusters can also be obtained by a pretreatment of 4 wt% precalcined Pd–mordenite under N_2 at high temperature, leading to a dark-grey powder. Hence the N_2 pretreatment can be considered an autoreduction. Indeed, whether a H_2 reduction or a N_2 autoreduction is applied for the pretreatment of 4 wt% Pd^0–mordenite, similar XRD diffractograms are recorded (Fig. 1f) and the same broad absorption is observed in the reflectance spectra. Despite these similarities, the Pd^0 particle dimension is clearly influenced by the reduction conditions. For room temperature reduction under H_2, TEM analysis reveals generally spherical or rectangular Pd^0 clusters with a dimension of 50–150 nm (Fig. 2b). On the other hand, an autoreduction pretreatment contributes to a large fraction of small (2–5 nm) Pd^0 clusters, as illustrated in Fig. 2c, although the picture also shows some large Pd metal clusters (≥50 nm). In any case (0.4 or 4 wt% Pd^0–mordenite) the large Pd^0 clusters clearly reside on the external surface of the zeolite. This is demonstrated by the SEM picture of 4 wt% Pd^0–mordenite (N_2) in Fig. 2d, where the white spots are surface-located Pd^0 clusters. Again, this trend is supported by rotation of the zeolite samples during TEM analysis, whereby the Pd^0 clusters pass over the surface.

Considering the XRD diffractograms shown in Fig. 1, one can conclude that the crystalline mordenite structure remains intact during the pretreatment conditions and even during Heck catalysis. Since no appreciable changes are noticed in comparison with the reference Na^+–mordenite, structural damage to the support seems unlikely.

Standard Reaction and General Reaction Characteristics

For evaluation of catalyst activity and stability, the Heck reaction between 4-bromoacetophenone and *n*-butyl acrylate at 130°C is chosen as a test reaction (Scheme 1). All Pd catalysts yield the main product *n*-butyl *trans*-3-(4-acetylphenyl)acrylate (Scheme 1, **I**) with a selectivity of more than 98%, as evidenced by liquid NMR of the isolated product. Results of GC–MS revealed the *cis*-compound (Scheme 1, **II**) as a minor product, while the 1,1-substituted product is not found in the reaction mixture.

Influence of the Reaction Conditions on Catalyst Heterogeneity

An optimization of the reaction conditions proved necessary to prevent Pd from leaching from the support. The effects of the nature of the base and the solvent were first considered for reactions with mordenite-based catalysts. With

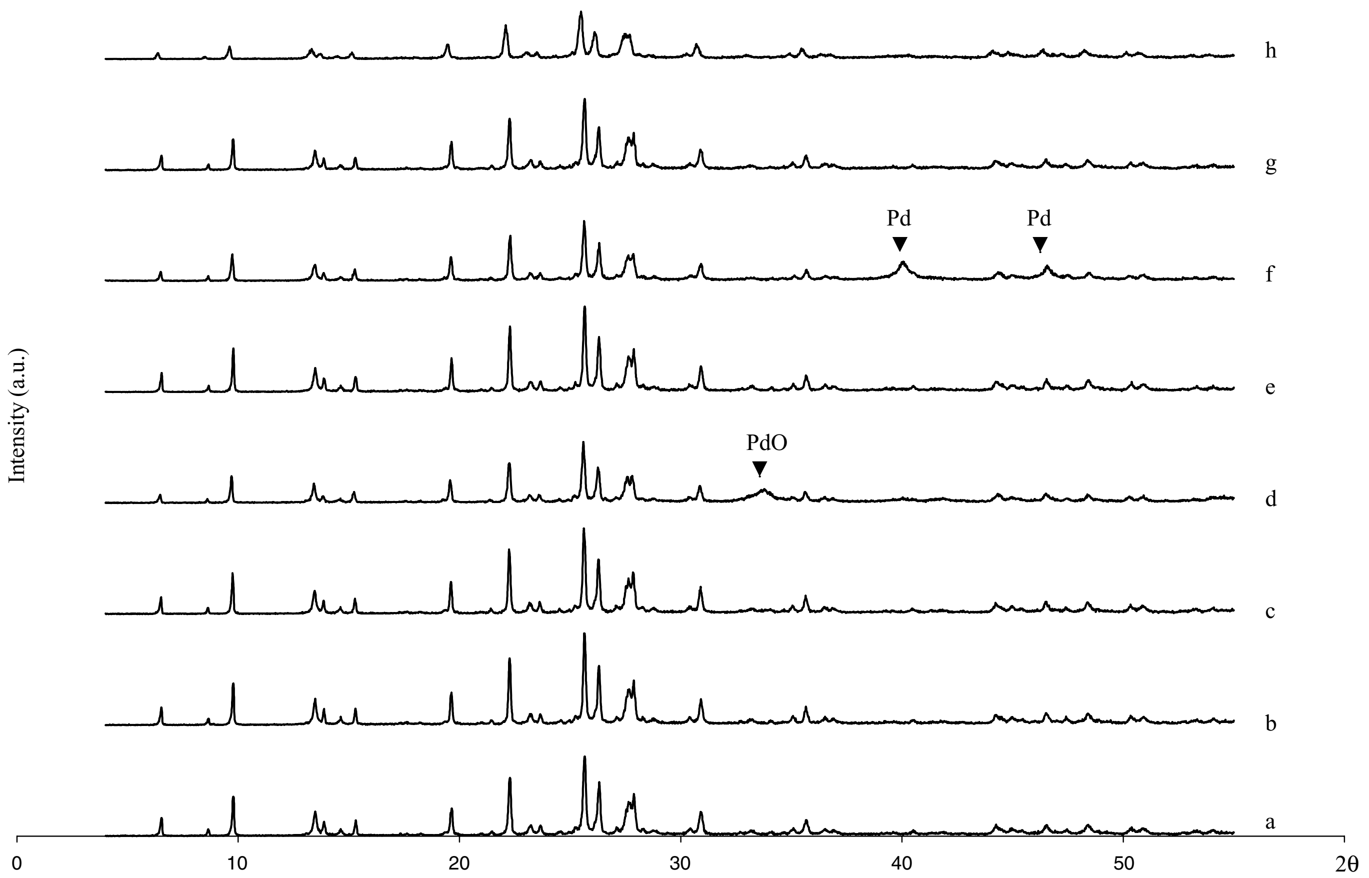


FIG. 1. X-ray diffractograms of (a) Na^+–mordenite, (b) $Pd(NH_3)_4^{2+}$–mordenite (4 wt%), (c) Pd^{2+}–mordenite (0.4 wt% Pd), (d) PdO–mordenite (4 wt% Pd), (e) Pd^0–mordenite (0.4 wt% Pd, H_2 reduction), (f) Pd^0–mordenite (4 wt% Pd, H_2 reduction), (g) $Pd(NH_3)_4^{2+}$–mordenite (0.4 wt%, after reaction), and (h) Pd^0–mordenite (0.4 wt% Pd, H_2 reduction, after reaction).

NaOAc as the base and Pd–mordenite catalysts, however, the conversion-time plots in Fig. 3a prove that the immobilized Pd species, both the $Pd(NH_3)_4^{2+}$ precursor and the Pd^0 clusters, are prone to leaching. Indeed, the filtrate test in Fig. 3a demonstrates that for 4 wt% Pd^0–mordenite the filtrate is not much less active than the suspension with the solid catalyst. However, for a 0.4 wt% $Pd(NH_3)_4^{2+}$ catalyst, in which the Pd is well distributed because of the competitive ion exchange, the acetate ions cause less leaching. As a result, only a moderate activity is found in the supernatant of a reaction with 0.4 wt% $Pd(NH_3)_4^{2+}$–mordenite.

In a next step, reactions were performed with tributylamine as the base instead of NaOAc, in DMA as the solvent. As can be observed in Fig. 3b, the catalytic reaction is only partly heterogeneous: apparently catalytically active Pd dissolves into DMA. Therefore, toluene was tested as a solvent instead of DMA. Even if the reaction with tributylamine in toluene is appreciably slower than in DMA, it is clear that these reactions are perfectly heterogeneous, as shown in Fig. 3c. With analogous organic bases like tripropylamine or tripentylamine, the same results are obtained: the reaction progresses smoothly, and the filtrates are free of activity. Additionally, no Pd leaching (<1% of the total Pd) could be detected by AAS experiments on the filtrates. However, when the alkyl groups on the amine are too large, as in trioctylamine, the Heck reaction is much retarded. This may be attributed to the sterical hindrance by the bulky alkyl groups, which limit the diffusion of the substrates to the active sites.

The reasons for leaching or stability of the Pd catalyst can be understood as follows. If the solution contains a large amount of acetate ions, these may form ion pairs with ionic Pd^{2+}. Particularly when the Pd concentration on the support is large, or when most Pd is located at the outer surface, as in the 4 wt% reduced Pd^0–mordenite, complexation of Pd^{2+} by acetate is a sufficient driving force to bring Pd^{2+} into solution. As to the solvents, aprotic highly polar solvents such as DMA, dimethylformamide (DMF), propylene carbonate, and acetone have often been used in homogeneous Heck reactions since they provide high rates. It is supposed that these solvents stabilize catalytically active Pd colloids against extensive agglomeration by forming a shell of coordinating solvent molecules around the clusters (14, 36). In reactions

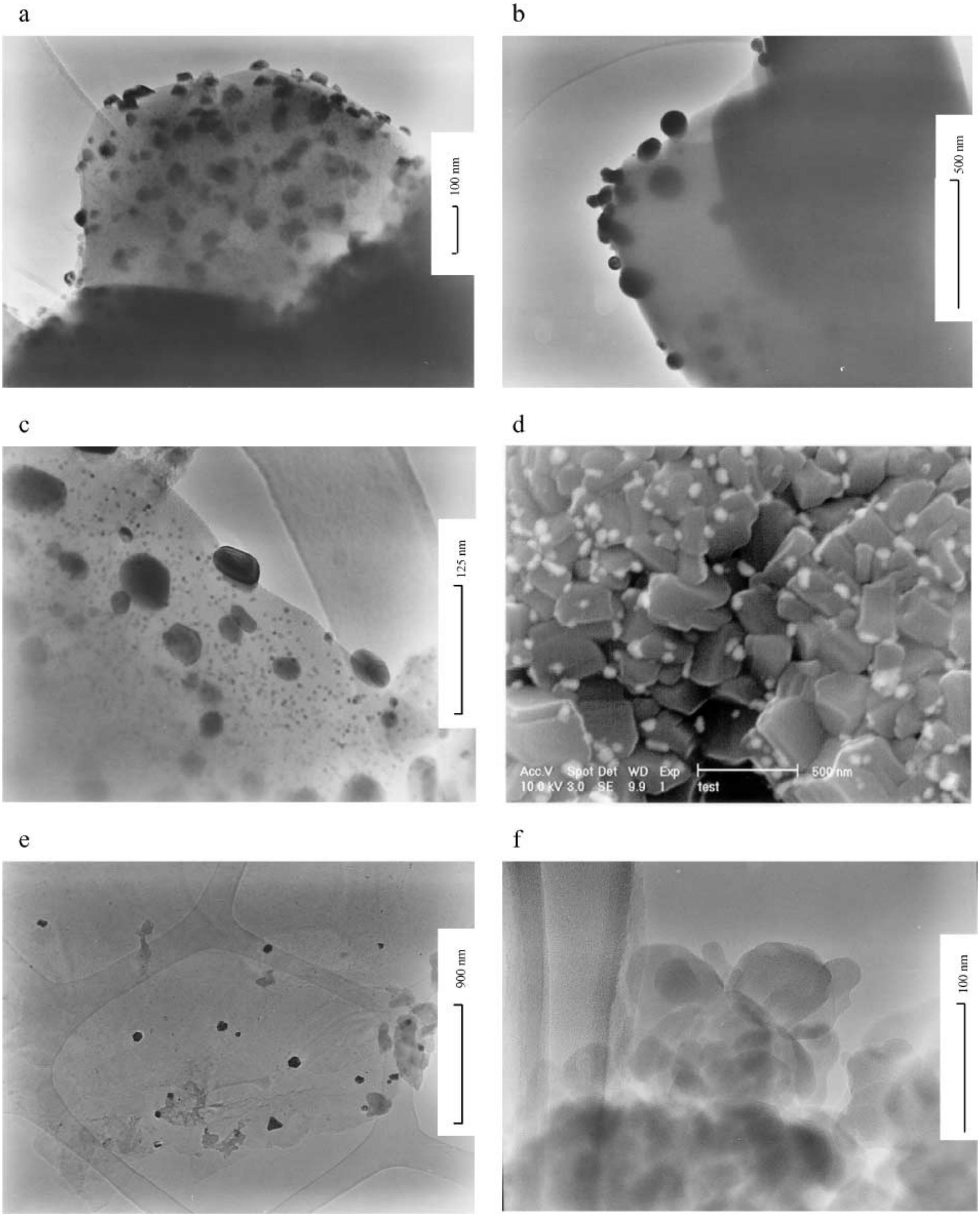


FIG. 2. (a) TEM of PdO–mordenite (4 wt% Pd), (b) TEM of Pd^0–mordenite (4 wt% Pd, reduction H_2), (c) TEM of Pd^0–mordenite (4 wt% Pd, reduction N_2), (d) SEM of Pd^0–mordenite (4 wt% Pd, reduction N_2), (e) TEM of $Pd(NH_3)_4^{2+}$–mordenite (0.4 wt% Pd) after reaction, and (f) TEM of $Pd(NH_3)_4^{2+}$–ZSM-5 (0.4 wt% Pd) during reaction.

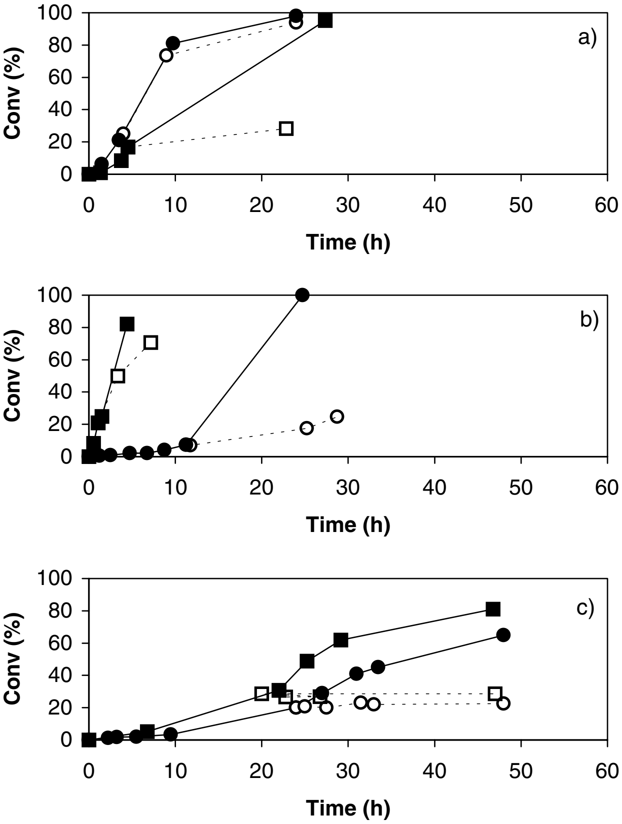


FIG. 3. The conversion of 4-bromoacetophenone in the suspension with the Pd–zeolite (solid symbols and lines) and in the filtrate after catalyst removal (open symbols and dotted lines) in function of time. (a) DMA and NaOAc, (b) DMA and $n\mathrm{Bu_3N}$, and (c) toluene and $n\mathrm{Bu_3N}$. Other reaction conditions: 4-bromoacetophenone, n-butyl acrylate, 130°C. Catalysts: 100 mg $\mathrm{Pd(NH_3)_4^{2+}}$–mordenite (0.4 wt% Pd) (■, □), or 10 mg $\mathrm{Pd^0}$–mordenite (4 wt% Pd) (●, ○).

with Pd–mordenite in DMA and an amine base, the solvent is apparently able to remove Pd colloids from the zeolite and to stabilize them in solution. In contrast, the combination of tributylamine and toluene avoids conditions in which ionic $\mathrm{Pd^{2+}}$ or colloidal $\mathrm{Pd^0}$ may be extracted to the liquid phase.

In the view of previous work, Pd–mordenite is a heterogeneous Heck catalyst even when NaOAc is used as base in DMA (23). However, such conclusions largely depend on the definition of heterogeneous catalysis (cf. supra) and on the methods used for validating heterogeneity in solid–liquid heterogeneous catalysis (37). Neither recycling of the catalyst nor monitoring the filtrate activity *after reaction completion* can truly exclude the participation of dissolved Pd species in the catalytic activity. In catalyst reuse experiments, the solid might function as a quasi inexhaustible reservoir of leachable Pd species; even sub-parts-per-million concentrations of Pd may suffice for activity. Second, if filtrates of a *completed* reaction are studied, as in the work of Djakovitch and co-workers (23–26), the homogeneous Pd species might be recaptured on the support at the reaction end, as observed by Arai and coworkers (27, 28). Moreover, at the end of a reaction, when the aryl bromide substrate is nearly exhausted, catalytically active Pd particles might be deactivated. In order to know which Pd species are active during catalysis, the filtrate should be collected from the suspension while the reaction is still progressing, e.g., at 10 or 20% conversion; moreover, the filtrate should be taken from a hot suspension and under inert atmosphere. In this way, the filtrate test becomes extremely sensitive, since it detects even sub-parts-per-million levels of active Pd.

Summarizing, the result with Pd–mordenite in toluene and with tributylamine as base convincingly shows that Pd–zeolites can function in proper conditions as truly heterogeneous catalysts for Heck reactions. So, the whole reaction is catalyzed by Pd species immobilized in or on the zeolite support and not by Pd species dissolved in the reaction medium.

Comparison of Zeolite Supports with Carbon and SiO_2

Since in the catalytic Heck reaction the Pd continuously switches between the zerovalent and divalent states, the support material should have sufficient affinity for both these states. Figure 4 demonstrates that choosing the right type of support material for the Pd is crucial for obtaining heterogeneous catalysis. With the classical Pd/C catalyst (5, 28), active filtrates are obtained in the same conditions (toluene, tributylamine) for which Pd–mordenite is a heterogeneous catalyst. For $\mathrm{Pd/SiO_2}$ (4 wt% Pd), the activity is

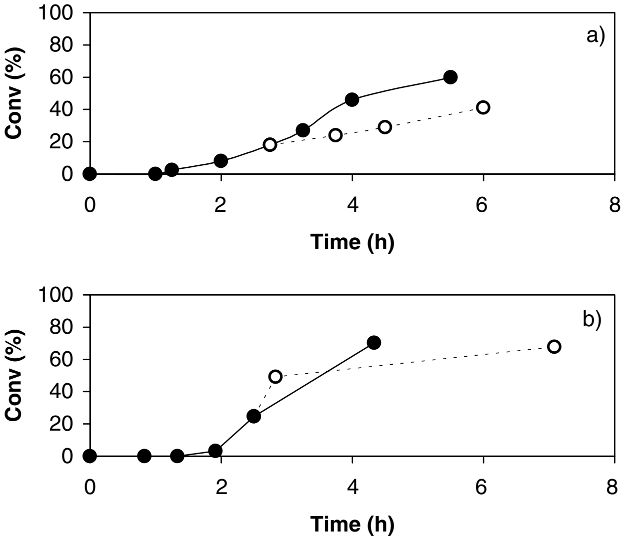


FIG. 4. The conversion of 4-bromoacetophenone in the suspension with the Pd catalyst (solid symbols and lines) and in the filtrate after catalyst removal (open symbols and dotted lines) in function of time. (a) 8 mg Pd/C (5 wt% Pd), (b) 10 mg $\mathrm{Pd/SiO_2}$ (4 wt% Pd). Reaction conditions: as in Fig. 3c, with toluene as the solvent and $n\mathrm{Bu_3}$ as the base, and with 0.125 mol% Pd catalyst with respect to aryl bromide.

even slightly higher in the filtrate than in the suspension. An obvious explanation for the difference between C and SiO_2 on one hand, and a zeolite such as mordenite on the other hand, is that the cation exchange properties of the zeolite allow better retention of the ionic forms of Pd. Since C or SiO_2 have only a small charge, their affinity for Pd^{II} is weak and under the operational Heck conditions Pd leaching is inevitable.

Influence of Pd Speciation and Loading on the Zeolite-Catalyzed Heck Reaction

In order to understand the effect of metal speciation on the heterogeneity and the rate of the reaction, different pretreatments were compared, with mordenite as the model support. In the reactions of Fig. 5, the total amount of Pd in the reaction is kept constant, but the metal is either present in a 4 wt% loading on a small catalyst mass (10 mg) or in a lower 0.4 wt% loading on a larger support mass. Satisfactory heterogeneity is obtained when the reaction is started with 100 mg 0.4 wt% $Pd(NH_3)_4^{2+}$–mordenite (Fig. 5a). Moreover, the reaction is much faster than with 10 mg 4 wt% $Pd(NH_3)_4^{2+}$–mordenite. At 34% conversion of 4-bromoacetophenone, the total Pd content in the filtrate amounts to only 72 ppb (±7 ppb), as evidenced by ICP. In contrast, with the 4 wt% $Pd(NH_3)_4^{2+}$–mordenite, leaching is detected, even if the amount of $Pd(NH_3)_4^{2+}$ exchanged on the zeolite (0.75 meq g^{-1}) is still appreciably lower than the CEC (2.7 meq g^{-1}).

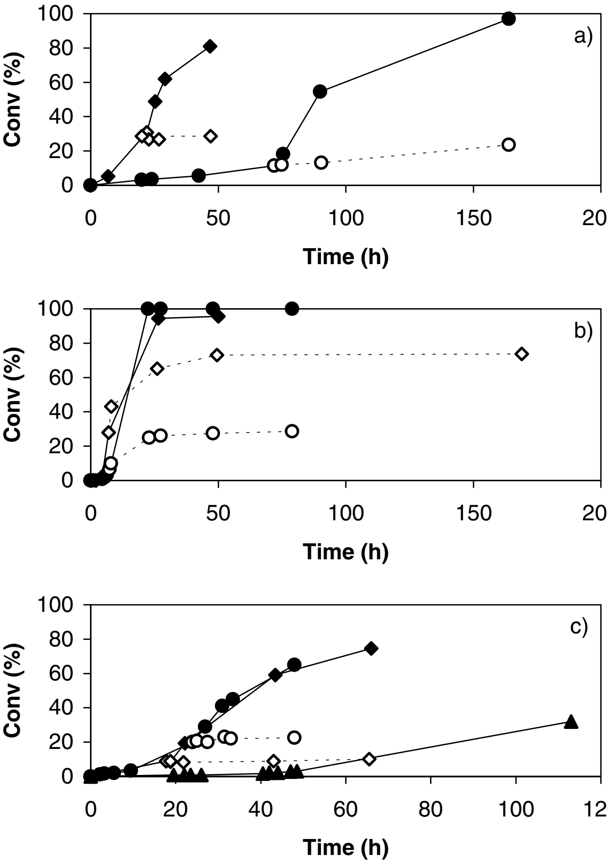


FIG. 5. The conversion of 4-bromoacetophenone in the suspension with the Pd–zeolite (solid symbols and lines) and in the filtrate after catalyst removal (open symbols and dotted lines), with 100 mg Pd–mordenite (0.4 wt% Pd) (◆, ◇) or 10 mg Pd–mordenite (4 wt% Pd) (●, ○, ▲): (a) $Pd(NH_3)_4^{2+}$–mordenite, (b) calcined Pd–mordenite, and (c) reduced Pd–mordenite. In (c) samples were reduced with H_2 at RT (◆, ◇, ▲) or with N_2 at 500°C (●, ○). Other reaction conditions as in Fig. 3c.

In the calcination of the $Pd(NH_3)_4^{2+}$-exchanged mordenites, the complexes are oxidized to isolated Pd^{2+} ions in 0.4 wt% Pd–mordenite or to surface-located PdO clusters in 4 wt% Pd–mordenite. However, both Pd^{II} species cannot be withheld by the mordenite in the present reaction conditions (Fig. 5b). Palladium with a coordination sphere full of oxygen atoms is obviously most prone to leaching; the comparison with the well-retained $Pd(NH_3)_4^{2+}$ ions shows that the presence of amine ligands much improves the metal retention.

Reduction of 0.4 wt% Pd–mordenite (H_2, RT) or autoreduction (N_2, 500°C) of 4 wt% Pd–mordenite leads again to fully heterogeneous catalysts for reactions with tributylamine in toluene (Fig. 5c). Since residual Pd^{II} species are expected to be very susceptible to leaching (Fig. 5b), the reduction must be fairly complete to eliminate even traces of Pd^{II}. Meanwhile, a too-drastic reduction and formation of large clusters must be avoided. As was shown by the TEM images of the zeolites reduced under N_2 or H_2, the N_2 autoreduction gives a much larger number of very small Pd^0 particles. This higher Pd dispersion results in a much higher activity for the autoreduced zeolite than for the H_2 reduced catalyst, as shown in Fig. 5c.

Summarizing, in order to obtain a heterogeneous catalyst, it seems sufficient to avoid conditions in which all oxygen-coordinated Pd^{II} is present on the mordenite. This can be achieved by appropriate reduction, or by starting from tetramine Pd complexes. While it is probable that at least part of the amine ligands must be removed from $Pd(NH_3)_4^{2+}$ in order to create vacant coordination sites for incoming reactants, the satisfactory retention of Pd–amine species can obviously be related to the higher ion exchange selectivity of amine complexes in comparison to bare Pd^{II} ions, particularly at low exchange levels (38, 39). That the $Pd(NH_3)_4^{2+}$ ions are slowly transformed to other species during the reaction is also evident from TEM evaluation of the 0.4 wt% $Pd(NH_3)_4^{2+}$–mordenite during and after reaction. Before reaction, no metallic features are observed in the matrix of crystalline mordenite, but during the reaction progress, the precursor is partially converted into Pd^0, and Pd^0 clusters can be observed as triangular or hexagonal plates, as shown in Fig. 2e. Thus, similar active species may well be formed, e.g., small Pd^0 particles, whether one starts from a Pd^0 or a $Pd(NH_3)_4^{2+}$ precursor; that the reaction conditions make the Pd converge toward similar active species

TABLE 3

The Conversion of 4-Bromoacetophenone in the Suspension and in the Filtrate after Catalyst Removal[a]

Entry	Catalyst	Pd content (wt%)[b]	Si/Al ratio	Additive[c]	Conversion (%)[d] (split time/h)	Conversion (%) (time/h)[d] Suspension	Conversion (%) (time/h)[d] Filtrate
1	$Pd(NH_3)_4^{2+}$–Y	0.4	2.71	/	32 (5)	82 (27)	34 (92)
2	$Pd(NH_3)_4^{2+}$–ZSM-5	0.4	18.6	/	9 (22)	66 (95)	9 (116)
3	$Pd(NH_3)_4^{2+}$–Mor	0.4	5.7	/	29 (20)	81 (47)	29 (47)
4	$Pd(NH_3)_4^{2+}$–Mor	0.4	6.47	/	32 (9.5)	85 (28)	38 (48)
5	$Pd(NH_3)_4^{2+}$–Mor	0.4	17.5	/	30 (8.3)	87 (29.5)	33 (48)
6	Pd^0–Mor[e]	4	5.7	/	20 (24)	65 (48)	22 (48)
7	Pd^0–Mor[e]	4	5.7	nBu$_4$NBr	12 (2.8)	57 (7.7), 83 (71)	13 (78)

[a] Reaction conditions: 4-bromoacetophenone, *n*-butyl acrylate, nBu$_3$N, toluene, and 130°C.

[b] 100 mg 0.4 wt% Pd catalyst and 10 mg 4 wt% Pd catalyst.

[c] 0.125 mmol nBu$_4$NBr.

[d] Conversion of 4-bromoacetophenone.

[e] Autoreduced by N_2.

is also indicated by the fact that for 0.4 wt% autoreduced Pd^0–mordenite and $Pd(NH_3)_4^{2+}$–mordenite, practically the same activity is observed (Figs. 5a and 5c).

Influence of the Zeolite Support

Knowing that a well-dispersed 0.4 wt% $Pd(NH_3)_4^{2+}$–mordenite is a suitable precursor for a heterogeneous catalyst with a high activity per Pd, the question arises as to whether other zeolites can be employed. Table 3 (entries 1, 2, and 3) shows catalytic data for $Pd(NH_3)_4^{2+}$–Y, $Pd(NH_3)_4^{2+}$–mordenite, and $Pd(NH_3)_4^{2+}$–ZSM-5 in the standard Heck reaction between 4-bromoacetophenone and *n*-butyl acrylate. All zeolites contain 0.4 wt% Pd; the rest of the CEC is occupied by Na^+. First, these data prove that not only mordenite but also Y and ZSM-5 are able to stabilize the Pd species and to restrain them from leaching, since there is no further conversion of 4-bromoacetophenone in the filtrate after the separation point. Besides, also leaching of inactive Pd species can be neglected: only 21 ppb Pd (±4 ppb) is detected by ICP. Second, for the heterogeneous catalysts with identical total Pd concentrations, structure clearly influences the activity in the following order:

$$Pd(NH_3)_4^{2+}\text{–Y} > Pd(NH_3)_4^{2+}\text{–mordenite} > Pd(NH_3)_4^{2+}\text{–ZSM-5}.$$

Obviously, the small pore dimensions of the MFI structure are expected to render the access to the well-dispersed $Pd(NH_3)_4^{2+}$ more difficult than for 12-MR zeolites such as Y and mordenite; analogously, the tridimensional channel network of Y gives less diffusion resistance than the monodimensional mordenite structure. TEM observation of these zeolites during catalysis shows that with $Pd(NH_3)_4^{2+}$–NaY, some Pd clusters are formed toward the end of the reaction, as for the mordenite catalyst. In contrast, no Pd metal particles can be distinguished at all in a used $Pd(NH_3)_4^{2+}$–NaZSM-5 catalyst (Fig. 2f), indicating that the highly dispersed Pd in the pore system is capable of performing the reaction.

The effects of various pretreatments were as well investigated for the other zeolite structures. In all cases, calcined zeolites were not at all heterogeneous. This confirms that Pd^{2+} or PdO are to be avoided. Use of zeolites reduced under N_2 or H_2 was only partly succesfull with respect to heterogeneity; this is probably due to the difficulty with which even the last oxidized Pd^{II} species can be reduced to metallic Pd. For instance, with reduced Pd–ZSM-5 or PdY, between 10 and 80% of the total activity is due to dissolved Pd species. Obviously, if Pd^{2+} is localized at energetically favorable lattice sites, it may not totally be reduced even in drastic conditions, and residual Pd^{II} may then cause metal leaching.

For the different $Pd(NH_3)_4^{2+}$-exchanged zeolites of Table 3 (entries 1, 2, and 3), the reaction rate increases as the Si/Al ratio of the supporting zeolites decreases. The influence of the Si/Al ratio on the activity is investigated in the reference reaction catalyzed by $Pd(NH_3)_4^{2+}$–mordenites with different Si/Al ratio (viz. 5.7, 6.47, 17.5; Table 3: entries 3, 4, and 5). The heterogeneity of all $Pd(NH_3)_4^{2+}$–mordenite catalysts is maintained in toluene and with tributylamine as base, independent of the Si/Al ratio; but the catalyzed reaction is faster for higher Si/Al ratios (e.g., 6.47, 17.5). However, this reaction acceleration must be attributed to the increasing mesoporosity of the mordenite structures with increasing Si/Al ratio. Desalumination of the mordenites by steaming contributes to structure defects and a more open zeolite structure. Therefore, also the differences in reactivity between the zeolite supports Y, mordenite, and ZSM-5 may be determined by the structure rather than by the Si/Al ratio.

Influence of Promoters on Induction Period and Reaction Rate

In all reactions, an induction period is observed during which the catalyst activity gradually increases. Since the first step in Heck catalysis is the oxidative addition of an aryl halide on a Pd^0 species (1), this delay may correspond to the formation of appropriate Pd^0 species, particularly if a Pd^{II} compound is used as a catalyst precursor. For SiO_2 impregnated with $Pd(OAc)_2$, the reduction may be due to thermolysis of the acetate ligands (14, 40); with $Pd(NH_3)_4^{2+}$-exchanged zeolites, the ammonia ligands or the reactants themselves may be used as reductants. Besides, the alkene substrate might also reduce the palladium(II) precursor in combination with some water. However, even when the Pd is initially present as zerovalent species, an induction period is still observed, e.g., for commercial Pd/C or reduced Pd–mordenite zeolites. This means that even other factors are responsible for the induction. An obvious possibility is that one of the reaction products, viz. the Heck coupling product, or the salt $NBu_3 \cdot HBr$ plays a role. In order to test the effect of quaternary ammonium salts, reactions were performed with nBu_4NBr as a promoter, with Pd^0–mordenite (4 wt% Pd, N_2 reduction) or $Pd(NH_3)_4^{2+}$–mordenite (0.4 wt% Pd) as the catalyst. In these conditions, the maximal reaction rate increases enormously and the induction period nearly disappears. In Table 3 (entries 6 and 7), data for a reaction with Pd^0–mordenite (4 wt% Pd, N_2 reduction) are shown; similar results are obtained for $Pd(NH_3)_4^{2+}$–mordenite (0.4 wt% Pd) as the catalyst. In addition, the heterogeneity of Pd–mordenites is also maintained in the standard Heck reaction: there is no catalytic activity in the filtrates. Similar beneficial effects were observed with other added salts, such as NH_4Br, $n Bu_4NHSO_4$, or $n Bu_4NI$.

Particularly in homogeneous Heck catalysis, promotion by quaternary ammonium compounds is commonly observed and may result from several effects: (i) if a salt such as NaOAc is used as a base, the quaternary compound may solubilize the base (42–46); (ii) increased halide concentrations have been associated with increased rates, e.g., $PdBr^-$ is considered to be a reactive species toward oxidative addition; (iii) Pd colloids can be stabilized against agglomeration by a protecting layer of quaternary ammonium compounds (7, 40, 41). Since in the present reactions $n Bu_3N$ has been used as a base, enhanced base solubilization is not a factor in this case; however, it is probable that the quaternary ammonium compounds adsorb on the Pd clusters and thus stabilize them against excessive sintering (40, 41). In the Heck reaction catalyzed by 4 wt% Pd^0–mordenite the optimal concentration of NBu_4Br is about 110 mol per mol Pd. A smaller amount of the salt shows less influence on the induction period and on the reaction rate. When a higher concentration of the promoter is added, the reaction becomes slower again. First, the solubility of the quaternary ammonium salt in the toluene solvent may be exceeded; second, a too-high coverage of the surface of the Pd colloids may prevent surface reactions such as the oxidative addition of the bromoarene on Pd.

Continuous Heck Reaction

From the Heck reactions in batch reactors, it is clear that the catalytically active species of the $Pd(NH_3)_4^{2+}$–zeolites (0.4 wt% Pd) and of Pd^0–mordenite (4 wt% Pd) remain immobilized on the support during the whole course of the reaction, at the condition that the reactions are performed in toluene and with tributylamine as base. The advantage of such truly heterogeneous catalysts is that they can be applied in a continuous reactor. A mixture of 4-bromoacetophenone, *n*-butylacrylate, and tributylamine is dissolved in toluene and pumped upstream over a tube reactor filled with $Pd(NH_3)_4^{2+}$–Y (0.4 wt% Pd). In Figure 6, the evolution of the conversion of 4-bromoacetophenone in the effluent is given in function of time.

The reaction profile comprises three different stages: an incubation period, a sudden increase in the product yield, and a gradual decline to a steady-state level of 33% conversion. Since initially neither 4-bromoacetophenone nor tributylamine and only low amounts of *n*-butylacrylate are detected in the effluent, the reagents seem to adsorb on the catalyst in the initial phase. Probably Heck catalysis starts simultaneously with the adsorption. After approximately 12 h the *trans*-product is released from the catalyst bed with a yield of 87%, and the production of the Heck product decreases until a steady-state level of 33% conversion of 4-bromoacetophenone is reached, after 50 h. Eventually, the *trans*-cinnamate is produced at a rate of 3.5 g product per g Pd and per h.

Pd leaching from $Pd(NH_3)_4^{2+}$–Y (0.4 wt% Pd) to the effluent solution is determined in the course of the Heck

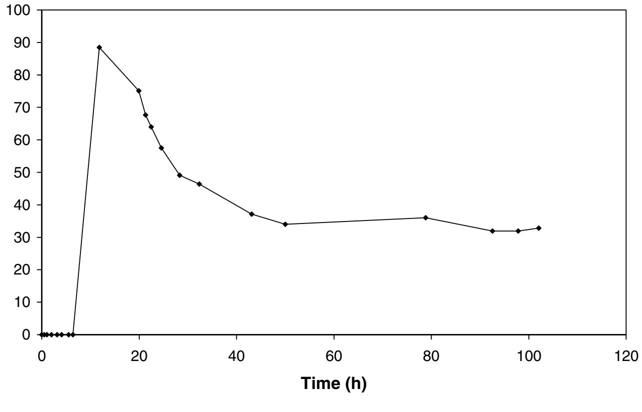


FIG. 6. The conversion of 4-bromoacetophenone in the effluent in function of time. The feed contains 4-bromoacetophenone, *n*-butyl acrylate, tributylamine, and toluene and is pumped (1.75 ml/h) upstream over a tube reactor (130°C), filled with 3.423 g $Pd(NH_3)_4^{2+}$–Y (0.4 wt% Pd, 500- to 800-μm particles).

TABLE 4

The Pd Concentration in the Effluent in Function of Time and Conversion of 4-Bromoacetophenone for the Continuous Experiment

Entry	Time (h)	Conversion (%)[a]	$[Pd]_{effluent}$ in ppm[b]
1	2	0	0.010
2	4	0	0.011
3	19.75	75	0.162
4	21.25	68	0.455
5	22	64	0.450
6	24.5	58	0.649
7	28.25	49	0.318
8	32.25	46	0.420
9	43	37	0.218
10	50.25	34	0.391
11	103	33	0.392

[a] Conversion of 4-bromoacetophenone in the effluent.

[b] Based on ICP results (±10%).

catalysis by ICP–OES measurements. Table 4 shows that only sub-parts-per-million levels of Pd are found in the effluent. Over the 103 h of the experiment, only 0.22% of the total Pd content is leached out.

This experiment confirms that the Pd–zeolites can be applied in a continuous reactor. Rescaling of the reactor dimensions and the flow may permit the production of the *trans*-Heck compounds on a larger scale.

CONCLUDING REMARKS

A study of the catalytic properties of Pd–zeolites in the Heck reaction of 4-bromoacetophenone with *n*-butyl acrylate shows that $Pd(NH_3)_4^{2+}$–zeolites (0.4 wt% Pd) and Pd^0–mordenite (0.4 and 4 wt% Pd) are not only active and selective but also *truly heterogeneous* catalysts, at the condition that the reaction is performed in toluene and with an amine as base. Filtrate tests did not give evidence for leaching of active Pd, while ICP analysis of the total Pd in the filtrates or reactor effluents proved that leaching of nonactive Pd was negligible as well (<1 ppm). The relation between leaching and catalyst pretreatment is clear now: particularly Pd^{II} in an all-oxygen environment is prone to leaching. Pd^{II}–amine species, and zerovalent Pd can be well retained on the support. Not only zeolites with large Pd^0 particles on the outer surface but also zeolites without such clusters, in which the Pd is highly dispersed, can act as truly heterogeneous Heck catalysts. An example of the latter class of catalysts is $Pd(NH_3)_4^{2+}$–ZSM-5, as was demonstrated by combined catalysis and TEM on the working catalyst. Obviously, pretreatments that result in higher dispersion, e.g., autoreduction with N_2 vs reduction with H_2, give a higher catalyst activity. Important promotion effects have been obtained by the addition of quaternary ammonium promoters to the heterogeneous Pd–zeolites. Finally, the heterogeneous catalyst $Pd(NH_3)_4^{2+}$–Y (0.4 wt% Pd) is successfully used in a continuous Heck experiment: a stable rate of 3.5 g product per g Pd and per h is reached and Pd leaching is hardly detectable.

With this insight in the catalytic properties of Pd–zeolites in Heck chemistry, further research focuses on Heck reactions with less reactive compounds, such as nonactivated bromoaromatics and chloroaromatics. Also, the suitability of the Pd–zeolites for related Pd chemistry will be investigated.

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