Pd–Zeolites as Heterogeneous Catalysts in Heck Chemistry

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INTRODUCTION

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 species and the PdII intermediates must be sufficiently stabilized on the zeolites against leaching and against aggregation to inactive Pd catalysts (Pd/C and Pd/SiO2) giving rise to Pd leaching as well. The heterogeneous nature of the catalysis largely depends on the pretreatment and on the solvent and base used. With tributylamine as the base and in toluene, the Heck olefinations with Pd(NH3)2+ ions, PdO particles, and Pd0 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(NH3)2+–zeolites (0.4 wt% Pd; mordenite, Y, ZSM-5) and Pd0–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 PdII in an all-oxygen environment, i.e., ionic Pd2+ or PdO. Supported Pd catalysts (Pd/C and Pd/SiO2) 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.
the vinylation of iodobenzene with methyl acrylate in the presence of Na₃CO₃/NET₃ 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 NH₄⁺–zeolites were converted to the Na⁺ form. To suspensions of H⁺–zeolites, a dilute ammonia solution was added dropwise until neutral pH. Next, the NH₄⁺–zeolites were suspended in water containing a fivelfold 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(NH₃)₄Cl₂. 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(NH₃)₄Cl₂ 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 O₂ at 500°C (1°C/min, 8 h at 500°C), Pd⁺⁺–zeolites are obtained. Pd⁰–zeolites are prepared by a pretreatment under N₂ at high temperature (12 h, 500°C) or by a H₂ reduction at room temperature of the oxidized Pd⁺⁺–zeolites. SiO₂ (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 CuKα radiation, λ = 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 |

<table>
<thead>
<tr>
<th>Support/catalyst</th>
<th>Counter ion</th>
<th>Origin</th>
<th>Overall Si/Al ratio</th>
<th>Crystal size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mordenite</td>
<td>Na⁺</td>
<td>Norton Zeolon 100</td>
<td>5.7</td>
<td>1.5–3.5</td>
</tr>
<tr>
<td>Mordenite</td>
<td>H⁺</td>
<td>Zeocat ZM510</td>
<td>6.47 (11⁺)</td>
<td>1–2</td>
</tr>
<tr>
<td>Mordenite</td>
<td>NH₄⁺</td>
<td>PQ Zeolites BV, CBV 30A</td>
<td>17.5</td>
<td>ND⁺</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Na⁺</td>
<td>Zeocat PZ-2/40</td>
<td>18.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Y</td>
<td>Na⁺</td>
<td>Zeocat</td>
<td>2.71</td>
<td>2–3</td>
</tr>
<tr>
<td>Pd/C (5 wt% Pd)</td>
<td>—</td>
<td>Johnson Matthey</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>SiO₂ (Kieselgel 60)</td>
<td>—</td>
<td>Fluka</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

* Based on SEM results.

b Bulk Si/Al ratio.

c ND, Not determined.
mixture consists of 3 mmol aromatic compound, 4.5 mmol vinyllating 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. 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 1H and 13C NMR measurements, including catalytically active and nonactive 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(NH3)4Cl2, the white color of the starting materials is maintained. The presence of Pd(NH3)42+ 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 PdII species obtained by calcination of Pd(NH3)42+-mordenite under O2 largely depends on the Pd concentration. The 0.4 wt% Pd–mordenite turns pink upon calcination; it contains isolated Pd2+ cations coordinated to lattice sites, as indicated by an absorption at 477 nm in the
Whether a H2 reduction or a N2 autoreduction is applied for pretreatment can be considered an autoreduction. Indeed, Pd(NH3)2Cl2 DAMS ET AL.

This is apparent from the external surface of the 4 wt% Pd0 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% Pd0–mordenite) the large Pd0 clusters clearly reside on the external surface of the zeolite. This is demonstrated by the SEM picture of 4 wt% Pd0–mordenite (N2) in Fig. 2d, where the white spots are surface-located Pd0 clusters. Again, this trend is supported by rotation of the zeolite samples during TEM analysis, whereby the Pd0 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

### 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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd contenta</th>
<th>Preparation, pretreatmentb</th>
<th>Pd species</th>
<th>Color</th>
<th>XRDc</th>
<th>UV–vis DRS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(OH3)2–MOR</td>
<td>0.4</td>
<td>CIE, calc</td>
<td>Pd(NH3)2+</td>
<td>White</td>
<td>MOR</td>
<td>299 (sh 230)</td>
</tr>
<tr>
<td>Pd(OH3)2–Y</td>
<td>0.4</td>
<td>CIE</td>
<td>Pd(NH3)2+</td>
<td>White</td>
<td>Y</td>
<td>299 (weak 223)</td>
</tr>
<tr>
<td>Pd(OH3)2–ZSM-5</td>
<td>0.4</td>
<td>CIE</td>
<td>Pd(NH3)2+</td>
<td>White</td>
<td>ZSM-5</td>
<td>299</td>
</tr>
<tr>
<td>Pd(OH3)2–MOR</td>
<td>4</td>
<td>IE</td>
<td>Pd(NH3)2+</td>
<td>White</td>
<td>MOR</td>
<td>299 (sh 230)</td>
</tr>
<tr>
<td>Pd0–MOR</td>
<td>0.4</td>
<td>CIE, calc</td>
<td>Pd0</td>
<td>Pink</td>
<td>MOR</td>
<td>477</td>
</tr>
<tr>
<td>Pd0–MOR</td>
<td>4</td>
<td>IE, calc</td>
<td>Pd0</td>
<td>Tobacco brown</td>
<td>MOR + 2θ = 34°</td>
<td>Broad</td>
</tr>
<tr>
<td>Pd0–MOR</td>
<td>0.4</td>
<td>CIE, calc, red (H2, RT)</td>
<td>Pd0</td>
<td>Bright grey</td>
<td>MOR</td>
<td>Broad</td>
</tr>
<tr>
<td>Pd0–MOR</td>
<td>4</td>
<td>IE, calc, red (H2, 500°C)</td>
<td>Pd0</td>
<td>Dark grey</td>
<td>MOR + 2θ = 40° + 2θ = 47°</td>
<td>Broad</td>
</tr>
<tr>
<td>Pd0–MOR</td>
<td>4</td>
<td>IE, calc, red (H2, RT)</td>
<td>Pd0</td>
<td>Black</td>
<td>MOR + 2θ = 40° + 2θ = 47°</td>
<td>Broad</td>
</tr>
<tr>
<td>Commercial Pd/C</td>
<td>5</td>
<td>—</td>
<td>Pd0</td>
<td>Black</td>
<td>2θ = 40°</td>
<td>Broad</td>
</tr>
<tr>
<td>Pd/SiO2</td>
<td>4 Impregnation</td>
<td>Pd0</td>
<td>Black</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

a Weight percent, verified by AAS.
b CIE, Competitive ion exchange; IE, ion exchange; calcination, red, reduction.
c Zeolite phase – other reflections.
d 2θ = 34°, plane 101 of PdO.
e 2θ = 40°, plane 111 of Pd0; 2θ = 47°, plane 200 of Pd0.
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\textsuperscript{0}–mordenite (4 wt% Pd, reduction H\textsubscript{2}), (c) TEM of Pd\textsuperscript{0}–mordenite (4 wt% Pd, reduction N\textsubscript{2}), (d) SEM of Pd\textsuperscript{0}–mordenite (4 wt% Pd, reduction N\textsubscript{2}), (e) TEM of Pd(NH\textsubscript{3})\textsubscript{2}\textsuperscript{+}–mordenite (0.4 wt% Pd) after reaction, and (f) TEM of Pd(NH\textsubscript{3})\textsubscript{2}\textsuperscript{+}–ZSM-5 (0.4 wt% Pd) during reaction.
Pd–zeolites as heterogeneous catalysts in Heck chemistry

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 co-workers (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 SiO2

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 Pd/SiO2 (4 wt% Pd), the activity is
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$_3$)$_2$$^{2+}$-mordenite (Fig. 5a). Moreover, the reaction is much faster than with 10 mg 4 wt% Pd(NH$_3$)$_2$$^{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$)$_2$$^{2+}$-mordenite, leaching is detected, even if the amount of Pd(NH$_3$)$_2$$^{2+}$ exchanged on the zeolite (0.75 meq g$^{-1}$) is still appreciably lower than the CEC (2.7 meq g$^{-1}$).

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.

![FIG. 5.](image-url)

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$_3$)$_2$$^{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.
is also indicated by the fact that for 0.4 wt% autoreduced Pd\textsuperscript{0}–mordenite and Pd(NH\textsubscript{3})\textsuperscript{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\textsubscript{3})\textsuperscript{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\textsubscript{3})\textsuperscript{2+}–Y, Pd(NH\textsubscript{3})\textsuperscript{2+}–mordenite, and Pd(NH\textsubscript{3})\textsuperscript{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\textsuperscript{+}. 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:

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

Obviously, the small pore dimensions of the MFI structure are expected to render the access to the well-dispersed Pd(NH\textsubscript{3})\textsuperscript{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\textsubscript{3})\textsuperscript{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\textsubscript{3})\textsuperscript{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\textsuperscript{2+} or PdO are to be avoided. Use of zeolites reduced under N\textsubscript{2} or H\textsubscript{2} was only partly successful with respect to heterogeneity: this is probably due to the difficulty with which even the last oxidized Pd\textsuperscript{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\textsuperscript{2+} is localized at energetically favorable lattice sites, it may not totally be reduced even in drastic conditions, and residual Pd\textsuperscript{II} may then cause metal leaching.

For the different Pd(NH\textsubscript{3})\textsuperscript{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\textsubscript{3})\textsuperscript{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\textsubscript{3})\textsuperscript{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.

### Table 3

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Pd content (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Si/Al ratio</th>
<th>Additive&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Conversion (%)&lt;sup&gt;d&lt;/sup&gt; (split time/h)</th>
<th>Conversion (%) (time/h)&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td>Suspension</td>
<td>Filtrate</td>
</tr>
<tr>
<td>1</td>
<td>Pd(NH\textsubscript{3})\textsuperscript{4+}–Y</td>
<td>0.4</td>
<td>2.71</td>
<td>/</td>
<td>32 (5)</td>
<td>82 (27)</td>
</tr>
<tr>
<td>2</td>
<td>Pd(NH\textsubscript{3})\textsuperscript{4+}–ZSM-5</td>
<td>0.4</td>
<td>18.6</td>
<td>/</td>
<td>9 (22)</td>
<td>66 (95)</td>
</tr>
<tr>
<td>3</td>
<td>Pd(NH\textsubscript{3})\textsuperscript{4+}–Mor</td>
<td>0.4</td>
<td>5.7</td>
<td>/</td>
<td>29 (20)</td>
<td>81 (47)</td>
</tr>
<tr>
<td>4</td>
<td>Pd(NH\textsubscript{3})\textsuperscript{4+}–Mor</td>
<td>0.4</td>
<td>6.47</td>
<td>/</td>
<td>32 (9.5)</td>
<td>85 (28)</td>
</tr>
<tr>
<td>5</td>
<td>Pd(NH\textsubscript{3})\textsuperscript{4+}–Mor</td>
<td>0.4</td>
<td>17.5</td>
<td>/</td>
<td>30 (8.3)</td>
<td>87 (29.5)</td>
</tr>
<tr>
<td>6</td>
<td>Pd\textsuperscript{0}–Mor&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4</td>
<td>5.7</td>
<td>nBu\textsubscript{4}NBr</td>
<td>20 (24)</td>
<td>65 (48)</td>
</tr>
<tr>
<td>7</td>
<td>Pd\textsuperscript{0}–Mor&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4</td>
<td>5.7</td>
<td>nBu\textsubscript{4}NBr</td>
<td>12 (2.8)</td>
<td>57 (7.7), 83 (71)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 4-bromoacetophenone, n-butyl acrylate, nBu\textsubscript{4}N, toluene, and 130°C.

<sup>b</sup> 100 mg 0.4 wt% Pd catalyst and 10 mg 4 wt% Pd catalyst.

<sup>c</sup> 0.125 mmol nBu\textsubscript{4}NBr.

<sup>d</sup> Conversion of 4-bromoacetophenone.

<sup>e</sup> Autoreduced by N\textsubscript{2}. 

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**Pd–ZEOLITES AS HETEROGENEOUS CATALYSTS IN HECK CHEMISTRY 233**
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 Pd⁰ species (1), this delay may correspond to the formation of appropriate Pd⁰ species, particularly if a Pd⁰ compound is used as a catalyst precursor. For SiO₂ impregnated with Pd(OAc)₂, the reduction may be due to thermolysis of the acetate ligands (14, 40); with Pd(NH₃)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 NB₄⁺ plays a role. In order to test the effect of quaternary ammonium salts, reactions were performed with nBu₄NBr as a promoter, with Pd⁰-mordenite (4 wt% Pd, N₂ reduction) or Pd(NH₃)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 Pd⁰-mordenite (4 wt% Pd, N₂ reduction) are shown; similar results are obtained for Pd(NH₃)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 NH₄Br, nBu₄NHSO₄, or nBu₄NI.

Particularly in homogeneous Heck catalysis, promotion by quarternary ammonium compounds is commonly observed and may result from several effects: (i) if a salt such as NaOAc is used as a base, the quarternary compound may solubilize the base (42–46); (ii) increased halide concentrations have been associated with increased rates, e.g., PdB⁺ is considered to be a reactive species toward oxidative addition; (iii) Pd colloids can be stabilized against agglomera-
tion by a protecting layer of quaternary ammonium compounds (7, 40, 41). Since in the present reactions nBu₄N has been used as a base, enhanced base solubilization is not a factor in this case; however, it is probable that the quarternary ammonium compounds adsorb on the Pd clusters and thus stabilize them against excessive sintering (40, 41). In the Heck reaction catalyzed by 4 wt% Pd⁰⁻mordenite the optimal concentration of NB₄Br 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 quarternary 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(NH₃)₂⁺⁺⁻zeolites (0.4 wt% Pd) and of Pd⁰⁻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(NH₃)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.

Figure 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(NH₃)₂⁺⁺⁻Y (0.4 wt% Pd, 500- to 800-μm particles).
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(NH₃)₂⁺–zeolites (0.4 wt% Pd) and Pd⁰–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 Pd⁰ in an all-oxygen environment is prone to leaching. Pd⁰ amine species, and zerovalent Pd can be well retained 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(NH₃)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 N₂ vs reduction with H₂, give a higher catalyst activity. Important promotion effects have been obtained by the addition of quaternary ammonium promotors to the heterogeneous Pd–zeolites. Finally, the heterogeneous catalyst Pd(NH₃)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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