Impact of Pd-mordenite pretreatment on the heterogeneity of Heck catalysis†

M. Dams, L. Drijkoningen, D. De Vos and P. Jacobs*

Kasteelpark Arenberg 23, 3001 Leuven, Belgium. E-mail: pierre.jacobs@agr.kuleuven.ac.be

In Heck reactions with tributylamine as the base and in toluene, $Pd(NH_3)_4^{2+}$-mordenite (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, while oxidized Pd^{II} species in an all-oxygen environment, *i.e.* ionic Pd^{2+} or PdO, are prone to leaching.

The Pd-catalyzed arylation or vinylation of olefins, universally known as the 'Heck reaction', is a versatile tool for the generation of new C–C bonds in a single step.[1] Advantages of Heck chemistry are the high selectivity, the tolerance of nearly any functional group on the substrates and the mild reaction conditions, associated with moderate toxicity and low cost of the reagents.[2] As an intriguingly flexible reaction it offers considerable potential in the organic synthesis of polyfunctional compounds, *e.g.* dienes, cinnamic esters and other variously substituted olefinic compounds.[3]

For economic reasons, industrial applications of homogeneous Heck reactions are limited.[4] Development of a suitable and re-usable heterogeneous catalyst remains therefore an important goal. Since Pd switches between the zerovalent and the divalent state in the catalytic Heck cycle, the choice of the support is crucial for retaining both states. Ying and coworkers reported on highly dispersed Pd in a mesoporous silica.[5] Although this solid catalyst was characterized by excellent activity and no Pd leaching, recycling was hampered by degradation of the structure. From commercially available Pd/C, Pd was found to leach into solution and to perform homogeneous catalysis.[6] Interestingly, almost all dissolved Pd^0 species can readsorb onto the surface of the carbon support after completion of the reaction. Evidently, such a pseudo-heterogeneous catalyst would fail in a continuous reactor. Ionic as well as neutral Pd species, entrapped in NaY and mordenite-type zeolites, were found to leach only significantly from the Y zeolite.[7] However, the severity of the leaching test used may seriously affect such conclusions.

The aim of this work is to find the relation between the nature of Pd species in mordenite and their ability to catalyze truly heterogeneous Heck chemistry. This implies that a clear discrimination must be made between dissolved and zeolite-associated activity. 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, as clearly evidenced by Arai and coworkers.[6] Therefore, the filtrate should be collected from the suspension while the reaction is still progressing, *e.g.* at 10 or 20% conversion;[8] 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-ppm levels of active Pd. In addition, the total Pd content in the filtrate is detected by AAS, including catalytically inactive Pd species.

Na-mordenite (Norton Zeolon 100, Si/Al = 5.7, crystal size 1.5–3.5 μm) with a CEC of 2.7 mequiv. g^{-1} was exchanged with an aqueous solution of $Pd(NH_3)_4Cl_2$ for 3 and 28%,

yielding mordenite with 0.4 and 4 wt% Pd, respectively. Both samples will be further denoted as 3PdNaMOR and 28PdNa-MOR, respectively. A competitive ion exchange procedure with a 25-fold molar excess of Na$^+$ w.r.t. Pd^{2+}, is conducted in order to obtain an adequate Pd distribution through the crystals.[9] The $Pd(NH_3)_4^{2+}$ cations absorb typically at approximately 299 nm in the DRS spectra.

The nature of the Pd^{II} species obtained by drying and *calcination* of the $Pd(NH_3)_4^{2+}$-mordenites under O$_2$ at 500 °C (1 °C min^{-1}, 8 h at 500 °C) largely depends on the Pd concentration. In 0.4 wt% Pd-mordenite isolated Pd^{2+} cations are coordinated to lattice sites, as indicated by an absorption at 477 nm in the DRS spectrum; while at 4 wt% Pd loading, large tobacco-brown PdO clusters are formed on the external surface and cause diffraction at $2\theta = 34°$ (plane 101) in the X-ray diffractogram.

Metallic Pd clusters are obtained by a H$_2$ *reduction* at room temperature, which results in a light grey and a black colour for 0.4 and 4 wt% Pd^0-mordenite, respectively. Pd^0-mordenite can also be obtained by *autoreduction*. A 4 wt% precalcined Pd-mordenite heated under N$_2$ at high temperature (12 h, 500 °C), leads to a dark grey powder. Comparable Pd^0 diffraction lines at $2\theta = 40°$ (plane 111) and at $2\theta = 47°$ (plane 200) are recorded in the X-ray diffractograms of 4 wt% Pd^0-mordenite, irrespective of the reduction conditions. Despite these similarities, TEM analysis visualizes the impact of the reduction conditions on the Pd^0 particle dimensions. TEM reveals the presence of spherical Pd^0 clusters with dimensions ranging from 50 to 150 nm for room temperature reduction under H$_2$, while an autoreduction pretreatment results in the formation of a large number of small Pd^0 clusters in the 2 to 5 nm range, accompanied by some large Pd metal clusters ($\geq$50 nm). In any case (0.4 as well as 4 wt% Pd^0-mordenite) SEM and TEM analyses prove that the large Pd^0 clusters clearly reside on the external surface of the zeolite.

To evaluate the effect of the valence and the coordination state of the metal on the heterogeneity and activity of the supported Pd-mordenites, the prepared catalysts are tested in the Heck reaction of 4-bromoacetophenone with n-butyl acrylate at 130 °C (Scheme 1). The reactions are performed in toluene and with tributylamine as the base, since earlier research has proven that Pd leaching occurs in an aprotic polar solvent, like DMA, or with an acetate as a base.[10] All Pd-mordenites yield *n*-butyl *trans*-3-(4-acetylphenyl)acrylate (**I**) with a selectivity of more than 98%, as evidenced by GC and liquid NMR of the isolated product, with the *cis*-isomer as minor product (**II**). Typically, the reaction‡ is followed until between 5 and 25% conversion is reached. At this moment (split time), the hot suspension is filtered (with 0.2 μm filter) and reaction progress is monitored in filtrate and catalyst suspension.
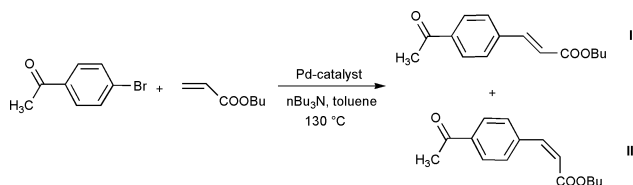
Scheme 1 Standard Heck reaction.

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† Electronic supplementary information (ESI) available: XRD patterns, TEM and SEM images. See http://www.rsc.org/suppdata/cc/b2/b201180h/

Catalysis with 100 mg of 3PdNaMOR is truly heterogeneous (Table 1, entry 1), since there is no catalytic activity in the filtrate after the split point and Pd leaching is not detected via AAS (< 1% of the total Pd content; less than 0.6 ppm). Besides, the reaction is much faster than with 10 mg 28PdNaMOR (same amount of Pd in the reactor, Table 1, entry 4). For the latter Pd leaching occurs, even though the amount of $Pd(NH_3)_4^{2+}$ exchanged is still appreciably lower than the CEC of the zeolite.

Whereas after calcination (Table 1, entries 2 and 5), an active system is generated, neither the isolated Pd^{2+} ions in 3PdNa-MOR, nor the surface located PdO clusters in 28PdNaMOR remain associated with the mordenite in the present reaction conditions, as the filtrate shows a significant conversion. In other reaction conditions, e.g. other solvents such as DMA or other bases such as NaOAc, leaching from calcined Pd zeolites was even much more pronounced.[10] Pd^{II} species with a coordination sphere full of oxygen atoms are clearly prone to leaching.

Hence, for the 3PdNaMOR catalysts, presence of amine ligands is required for satisfactory retention of cationic Pd, which can obviously be related to the higher affinity of $Pd(NH_3)_4^{2+}$ complexes for the mordenite crystals than that of bare Pd^{II} ions, particularly at low exchange levels (compare to the low but significant leaching for the untreated sample with high exchange degree; Table 1, entry 4).[11]

Reduction of the precalcined Pd-mordenites leads again to fully heterogeneous catalysts for reactions in toluene and with tributylamine as base (Table 1, entries 3 and 6). Since residual Pd^{II} species are expected to be very susceptible to leaching, this reduction must be fairly complete. Meanwhile, too drastic reduction and formation of large clusters must be avoided in order to keep a considerable activity. Our preliminary kinetic data show that the highly dispersed small Pd^0 particles formed in the autoreduction exhibit a superior catalytic activity in comparison with the hydrogen reduced catalyst 28PdNaMOR (Table 1, entries 6 and 7).

Thus, heterogeneous Heck catalysis is achieved by the exchange of tetramine Pd complexes on mordenite, possibly followed by an appropriate reduction, which avoids the presence of all-oxygen coordinated Pd^{II}. In the case of untreated 3PdNaMOR, TEM-examination of the zeolite samples during catalytic reaction shows small external Pd^0 particles, suggesting that at least part of the amine ligands must be removed from the $Pd(NH_3)_4^{2+}$ during the reaction progress.

As homogeneous Heck catalysis is promoted by the addition of quaternary ammonium salts,[4] the effect of Bu^n_4NBr is investigated in the reactions with 28PdNaMOR (N_2 reduction) and the untreated 3PdNaMOR. In presence of the promoter the reaction rate increases at least 5 times, the heterogeneity of the catalyst remaining unaffected. Similar beneficial effects were observed with other added salts, such as NH_4Br, $Bu^n_4NHSO_4$ or

Table 2 Catalytic results of Heck reactions catalyzed by autoreduced 28PdNaMOR in the presence of 0.413 mmol Bu^n_4NBr‡

Aryl halide	Olefin	Time[a]/h	Conv.[b] (%)	Sel.[c] (%)
Iodobenzene	n-Butyl acrylate	2	97	> 95
Bromobenzene	n-Butyl acrylate	51	5	> 95
Benzyl chloride[d]	n-Butyl acrylate	72	71	79
4-Bromoacetophenone	n-Butyl acrylate	20	80	> 95
4-Bromoacetophenone	n-Butyl crotonate	144	> 90	84
4-Bromoacetophenone	n-Butyl methacrylate	18	15	75
4-Bromoacetophenone	Styrene[e]	133	59	80

[a] Reaction time not optimized. [b] Conversion of the aryl halide. [c] Selectivity for the trans-compound. [d] 0.080 g catalyst. [e] no Bu^n_4NBr.

Bu^n_4NI. Although quaternary ammonium compounds contribute to several accelerating mechanisms,[4] it is probable that they adsorb on the Pd clusters under the reaction conditions and stabilize them against excessive sintering.[12] Due to this acceleration of Pd-mordenite catalysis, it is possible to broaden the reaction scope to less active reactants (Table 2).

This work highlighted the heterogeneity of $Pd(NH_3)_4^{2+}$ and Pd^0- mordenite in Heck catalysis, while oxidized Pd^{II} species in an all-oxygen sphere clearly leach into solution. Further work will prove the possibility to expand this well-defined catalytic system to other zeolite supports and to use the catalysts in related organic reactions.

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Table 1 Leaching tests in standard Heck reaction conditions‡ with 3PdNaMOR and 28PdNaMOR after different pretreatments[a]

Entry	Catalyst	Pretreatment	Conv. (%) (split time/h)	Conv. (%) (time/h) Suspension	Conv. (%) (time/h) Filtrate
1	3PdNaMOR	None	**31** (22)	81 (47)	**29** (47)
2	3PdNaMOR	Calcination	28 (7)	94 (26)	65 (26)
3	3PdNaMOR	Reduction	**9** (19)	75 (66)	**10** (65)
4	28PdNaMOR	None	11 (72)	97 (164)	24 (164)
5	28PdNaMOR	Calcination	7 (8)	100 (23)	29 (79)
6	28PdNaMOR	Autoreduction	**20** (24)	65 (48)	**22** (48)
7	28PdNaMOR	Reduction	32 (113)		

[a] See text.