Preparation of heterogeneous catalysts supported on mesoporous molecular sieves modified with various N-groups and their use in the Heck reaction

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ABSTRACT

A series of supported catalysts has been prepared from palladium(II) acetate and mesoporous molecular sieves bearing various N-donor groups at their surface and probed in the Heck coupling between *n*-butyl acrylate and bromobenzene to give *n*-butyl cinnamate. The results indicate that the catalytic activity as well as the amount of leached metal depends on the nature of the nitrogen modifying group. The best catalysts were obtained from the sieves bearing the $\equiv SiCH_2CH_2CH_2NH_2$ or $\equiv SiCH_2CH_2CH_2NHCH_2CH_2NEt_2$ groups at the surface. When combined with sodium acetate, the former catalyst provided the coupling product with conversions as high as 84% under microwave irradiation for 30 min and 84% under solvothermal conditions (160 °C/4 h) whereas application of the latter catalyst resulted in conversions 90% and 71% under identical reaction conditions (all at 1 mol% Pd loading). Conversions of 5% and 14%, respectively, were achieved with these catalysts under microwave conditions *without* an external base, which corresponds to the consumption of 77% and 88% amine sites by the liberated HBr. The particle growth leading to the catalyst deactivation was studied by high-resolution transmission electron microscopy and by X-ray powder diffraction.

1. Introduction

Heck reaction is a powerful synthetic tool for the construction of organic molecules via C–C bond coupling between aryl halides and alkenes [1]. Although many efficient catalytic systems have been reported in the literature, including those tailored for specific substrates and reaction conditions, the search for new catalytic systems is still challenging. The current catalyst design is mainly aimed at the development of catalysts that avoid elaborate (and often expensive) supporting ligands, could be re-used and are environmentally benign.
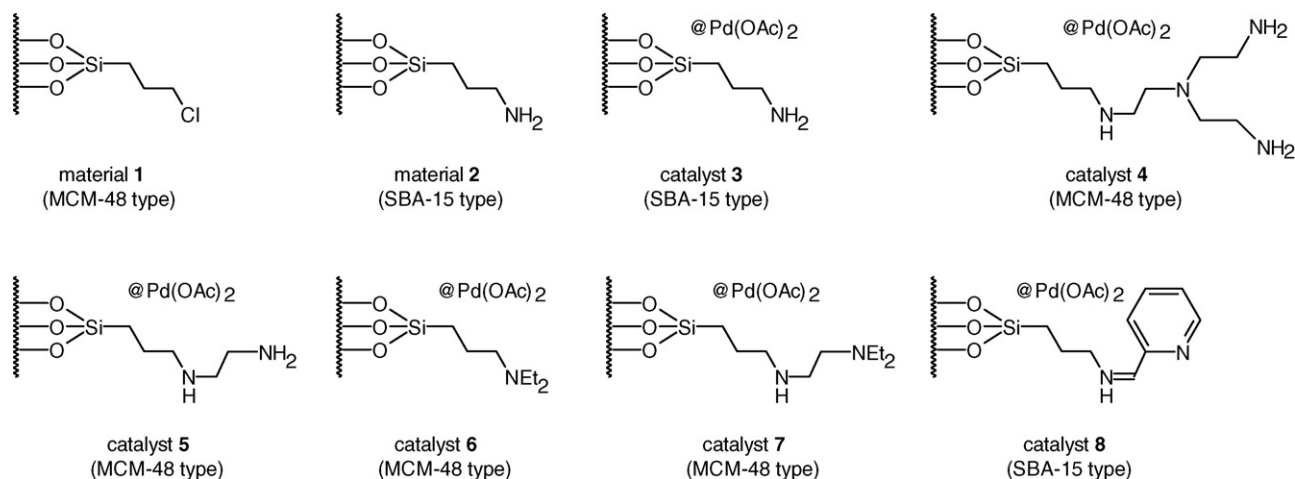
Ligand-free catalysts have been tested soon after the discovery of the Heck reaction [2]. Later on, it was found that the ligandless coupling proceeds more easily in the presence of additives that stabilise the palladium particles formed (nanoparticles) [3] via preventing their aggregation. The typical stabilising agents are tetraalkylammonium salts [4], polar solvents [5], polymers [6], and dendrimers [7]. Several research groups have deposited palladium

species also onto various solid supports [8]. Mesoporous molecular sieves of MCM-41 and SBA-15 types [8b,g,f] are among the most frequently tested supports because of their large surface areas, high thermal stability, narrow pore size distribution and well-defined ordered structure [9]. However, since the metallic particles often tend to leach from the support, it is advantageous to modify the solid matrix so as to provide an additional stabilisation of the metallic particles. Indeed, a number of palladium catalysts prepared by using siliceous supports modified with various N-containing organic groups has been reported in the literature [10]. The prominent examples include silica-bound Schiff bases [11] and molecular sieves possessing aliphatic amino or ammonium groups at their surface [12].

We found such materials particularly attractive since their properties might be easily tuned via modifying groups. In addition, the combination of palladium nanoparticles and basic sites capable of binding the acidic by-products can allow for the design of highly active bifunctional catalysts. In search of such materials, we have designed a series of palladium catalysts supported with aminoalkyl group-modified mesoporous molecular sieves. In this contribution, we report on the preparation and characterisation of these materials and results of their catalytic testing in the Heck reaction of *n*-butyl acrylate and bromobenzene.

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material **1**
(MCM-48 type)

material **2**
(SBA-15 type)

catalyst **3**
(SBA-15 type)

catalyst **4**
(MCM-48 type)

catalyst **5**
(MCM-48 type)

catalyst **6**
(MCM-48 type)

catalyst **7**
(MCM-48 type)

catalyst **8**
(SBA-15 type)

Scheme 1. The modified mesoporous molecular sieves studied.

2. Results and discussion

2.1. Preparation and characterisation of the catalysts

3-Chloropropyl- (cubic with MCM-48 type morphology; material **1**) and 3-aminopropyl-modified (SBA-15 type; material **2**) all-siliceous molecular sieves were prepared by direct template synthesis in a microwave oven using Pluronic tri-block copolymer as an organic template and sodium metasilicate as the silica source [13,14]. These sieves were subsequently converted to materials bearing pendant N-groups at the surface via alkylation reactions with the appropriate amine (for the 3-chloropropylated sieve) or by condensation with 2-pyridinecarboxaldehyde (3-aminopropylated sieve). The resulting materials were treated with palladium(II) acetate to give catalysts **3**–**8** (Scheme 1). For the sake of comparison, the series of catalysts was designed comprising the N-groups reported in the literature as well as newly prepared ones. From the modifying groups already established in the literature, we chose (2-pyridyl)imine (catalyst **8**) [11a–e,g], $-(CH_2)_3NH_2$ (catalyst **3**) [12b–e], $-(CH_2)_3NH(CH_2)_2NH_2$ (catalyst **5**) [12e,g], and $-(CH_2)_3NEt_2$ (catalyst **6**) [12d]. On the other hand, the newly introduced materials are those bearing the $-(CH_2)_3NH(CH_2)_2N[(CH_2)_2NH_2]_2$ (catalyst **4**) and $-(CH_2)_3NH(CH_2)_2NEt_2$ groups (catalyst **7**).

Since one of the main goals of this study was to find nitrogen groups that would not only stabilise active palladium species during the reaction but also bind the acidic by-products, our catalysts possessed an excess of nitrogen groups over the palladium to possibly ensure bifunctional reactivity. The (N-group)/Pd molar ratios ranged from 4.3 for catalyst **6** to 11.2 for catalyst **4** while the atomic N/Pd ratios were even higher for the catalysts bearing groups possessing two or more nitrogen atoms (catalysts **4**–**8**; see Table 1).

The resulting materials were characterised by elemental analysis, IR spectroscopy, powder X-ray diffraction, nitrogen adsorption isotherms and by high-resolution transmission electron microscopy (HR TEM). In all cases, the palladium content determined by ICP optical emission spectroscopy corresponded well to the amount of Pd(OAc)$_2$ added to the catalysts precursors, indicating practically quantitative deposition of palladium onto the support. Complementary information concerning the degree of surface exchange reaction in catalysts **4**–**7** was deduced from the chlorine content that corresponds to the amount of unreacted chloropropyl groups [15]. The low chlorine content in catalysts **5** and **7** implies that most of the 3-chloropropyl groups were converted into the respective nitrogen-containing ones (**5**: no Cl detected; **7**: less than ca. 10% Cl remained). By contrast, the extent of the exchange reaction in catalyst **6** as determined from chlorine and nitrogen contents was ca. 40%. This corresponds to a relatively lower reaction temperature compelled from the lower boiling point of the diethylamine educt.

X-ray diffraction patterns of the parent materials **1** and **2** and of catalyst **3** showed three or four peaks in the range $2\theta < 10°$ typical of ordered mesoporous molecular sieves. Although catalyst **3** exerted slightly lower diffraction intensities compared with the parent material **2** (probably due to its lower regularity), the diffraction data indicate that the support remains largely unchanged after deposition of palladium species. X-ray diffraction also provided valuable information about the growth of palladium nanoparticles (see below).

Nitrogen adsorption isotherms recorded for materials **1**–**8** all displayed a sharp increase in the adsorbed amount in the p/p_0 range of 0.6–0.8 characteristic of mesoporous molecular sieves with narrow pore size distributions (Fig. 1). The calculated textural parameters (Table 1) evidenced good quality and ordered structure of the materials. Material **1**, a cubic MCM-48 type mesoporous

Table 1
Analytical and textural characteristics of **1**–**8**.

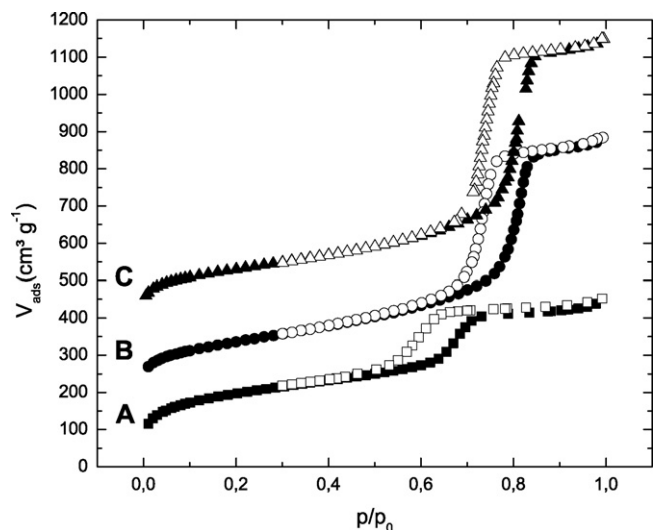| Sample	Pd content (mmol g^{-1})	N/Pd atom ratio	BET surface area (m^2 g^{-1})	Void volume (cm^3 g^{-1})	Pore size (nm)
Material **1**	–	–	700	0.95	6.2
Material **2**	–	–	495	1.27	8.0
Catalyst **3**	0.110	6.5	472	1.12	8.0
Catalyst **4**	0.099	44	219	0.43	5.0
Catalyst **5**	0.103	17	390	0.79	5.9
Catalyst **6**	0.093	4.3	424	0.67	5.3
Catalyst **7**	0.101	16	430	0.84	5.7
Catalyst **8**	0.103	12	381	1.01	8.1

Fig. 1. Nitrogen adsorption isotherms for material **1** (A), material **2** (B), and catalyst **3** (C). The isotherms for material **2** and catalyst **3** are shifted by 200 and 400 cm³ g⁻¹, respectively, to avoid overlapping.

molecular sieve [13], showed significantly larger surface areas and smaller pores than the hexagonal SBA-15 type material **2** [14]. In the case of SBA-15 type materials, the introduction of functional groups (**2** → **3** and **8**) led to a decrease in the surface area and void volume (the larger modifying group expectedly caused a more pronounced change), while the pore size remained practically the same. The textural properties MCM-48 type materials (**1** → **4**–**7**) followed similar though less regular trends.

FTIR spectra (Fig. 2) were rather inconclusive about the nature of Pd(OAc)₂–N-surface interaction, probably due to an excess of nitrogen groups as compared with the amount of anchored palladium. For instance, material **2** displayed a clearly discernible band of NH₂ scissoring vibration at 1594 cm⁻¹. Addition of palladium(II) acetate to material **2** resulted in a broad composite band between ca. 1500 and 1700 cm⁻¹ attributable to scissoring vibration of the NH₂ groups with a contribution from ν_{as}(CH₃CO₂) and the support. A band at 1413 cm⁻¹ with a shoulder at 1492 cm⁻¹ could be assigned to ν_s(CH₃CO₂), again with a contribution from the vibrational modes of the support.
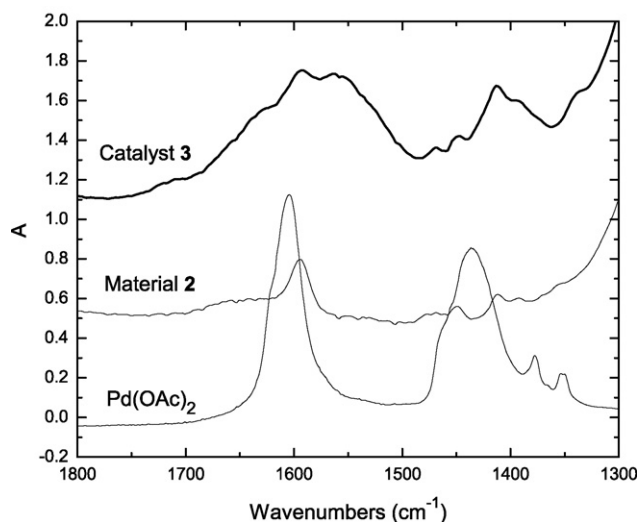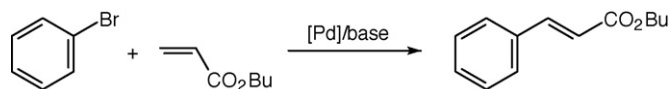

Fig. 2. FTIR spectra of catalyst **3**, its parent material **2** and Pd(OAc)₂ in Nujol mulls. For clarity, the spectra were shifted along the *A*-axis.

Scheme 2.

2.2. Catalytic tests

Catalytic activity of the prepared catalysts has been probed in the model Heck reaction between bromobenzene and *n*-butyl acrylate to give *n*-butyl cinnamate (Scheme 2). The reactions were carried out in *N,N*-dimethylacetamide (DMA) under microwave irradiation and conventional hydrothermal conditions. The catalytic tests were all performed at 1 mol% palladium loading and under similar conditions to allow for a direct assessment of the catalyst performance, namely of the influence of the surface-modifying groups. Materials containing no palladium did not exert any catalytic activity [16].

The results summarised in Table 2 reveal that all catalysts do not necessarily require the presence of an external base for the coupling to proceed: i.e., they are bifunctional. Yet, the amounts of the coupling product were rather low, always lower than the amount of the available base. For instance, the molar ratios *n*(butyl cinnamate)/*n*(N) were 0.69 for entry 1, 0.25 for entry 2, 0.88 for entry 3, and 0.42 for entry 4 (under microwave irradiation), and 0.28 for entry 13, 0.31 for entry 14, and 0.08 for entry 15 (under conventional heating). Apparently, the best results were obtained with catalyst **7** under microwave irradiation, where the conversion reached 14% in 30 min (entry 3 in Table 2) and most of the available base (N-atoms) was consumed (88% based on theoretical amount of liberated HBr). This catalyst also showed relatively low leaching of the metal component, corresponding to only 3% of the total Pd added to the reaction mixture (Table 3).

Generally, all the catalysts performed much better in the presence of anhydrous sodium acetate as the external base. The low conversions obtained with catalysts **4** and **5** (entries 7 and 8 in Table 2) can be tentatively attributed to an insufficient activation of the Pd source to active metal (Pd(II) → Pd(0)) under the reaction

Table 2
Summary of the catalytic results[a].

Entry	Catalyst	Conditions	Base	Conversion (%)[b]
1	**3**	MW, 30 min	–	5
2	**6**	MW, 30 min	–	1
3	**7**	MW, 30 min	–	14
4	**8**	MW, 30 min	–	5
5	**3**	MW, 30 min	+	84
6	**3**[c]	MW, 30 min	+	39
7	**4**	MW, 30 min	+	0
8	**5**	MW, 30 min	+	9
9	**6**	MW, 30 min	+	33
10	**7**	MW, 30 min	+	90
11	**7**[d]	MW, 30 min	+	34
12	**8**	MW, 30 min	+	94
13	**3**	T, 4 h	–	2
14	**7**	T, 4 h	–	5
15	**8**	T, 4 h	–	1
16	**3**	T, 4 h	+	84
17	**7**	T, 4 h	+	71
18	**8**	T, 4 h	+	57

[a] The reactions were performed under nitrogen atmosphere at 160 °C (solvothermal experiments, *T*) or 165 °C (microware irradiation, MW) with *n*-butyl acrylate (0.5 mmol), bromobenzene (0.75 mmol), sodium acetate as the base (0.75 mmol, if appropriate), mesitylene (internal standard, 0.42 mmol), DMA (2.5 mL) and catalyst (1 mol% with respect to *n*-butyl acrylate). For details, see Section 4.

[b] Determined by gas chromatography.

[c] 0.5 mol% Pd.

[d] Recycled catalyst **7** (from experiment no. 10).

Table 3
The amount of leached-out palladium.

Entry	Catalyst	Heating[a]	Pd in solution (ppm)	% total Pd
1	**3**	MW	23	11
2	**4**	MW	13	6
3	**5**	MW	Trace[b]	<1
4	**6**	MW	121	57
5	**7**	MW	7	s3
6	**8**	MW	107	50
7	**3**	*T* (hot)[c]	27	13
8	**3**	*T* (cold)[c]	18	8

[a] Heating for 30 min (MW) or 4 h (*T*).

[b] Below ca. 2.5 ppm (detection limit).

[c] The catalyst was filtered off before (hot) or after (cold) cooling of the reaction mixture using a syringe PTFE filter (declared pore size 0.45 μm).
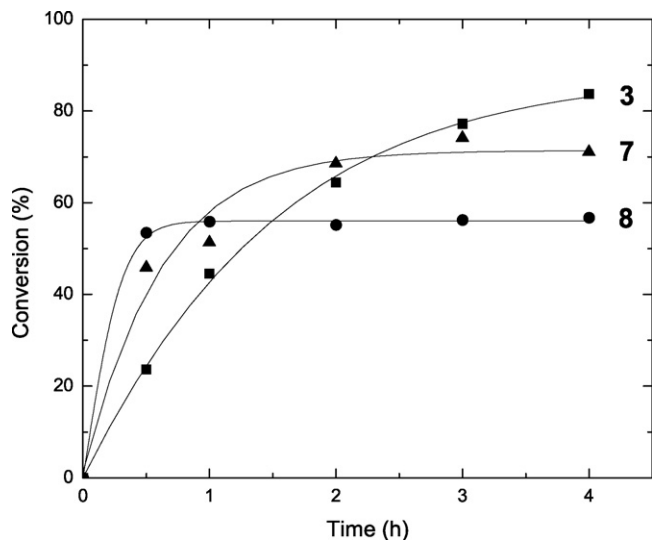

Fig. 3. Kinetic profiles of the coupling reaction with catalysts **3**, **7** and **8** under hydrothermal conditions (160 °C) in the presence of sodium acetate as the base.

Fig. 4. X-ray powder diffraction patterns of fresh catalyst **3** (bottom trace) and the sample recovered from the reaction mixture after conventional heating to 160 °C for 4 h (top trace).

strong Pd-support interactions limiting the amount of the available active metal in the reacting system.

The influence of the structure of the anchoring group is probably complex and may change in the presence and the absence of the external base. Nevertheless, the low amount of the leached metal from catalysts **4** and **5** suggests that not the number of nitrogen atoms in the anchoring group but rather their type is the decisive factor controlling the stabilisation (and availability) of the metal component. This can be demonstrated also in the pair of catalysts **3** and **6**. Whereas the use of catalyst **3** bearing only the primary amino groups resulted in 84% conversion, its congener possessing tertiary amine groups (–NEt$_2$) showed 33% conversion. The fact that the amounts of leached metal are just opposite, 11% for **3** and 57% for **6** (Table 2), seems to reflect a weaker Pd-surface (Pd-N) interaction in the latter case.

Apart from varying overall conversions, the catalyst exerted also different reaction rates. A comparison of kinetic profiles for the coupling reactions performed in the presence of sodium acetate (Fig. 3) reveal that catalyst **3** reacted relatively slowly but steadily,

conditions. This assumption is supported by visual observations as these materials either do not change their colour during the reaction or become only slightly greyish. Catalysts **4** and **5** also showed the lowest amounts of the leached-out metal. This could be a sign of
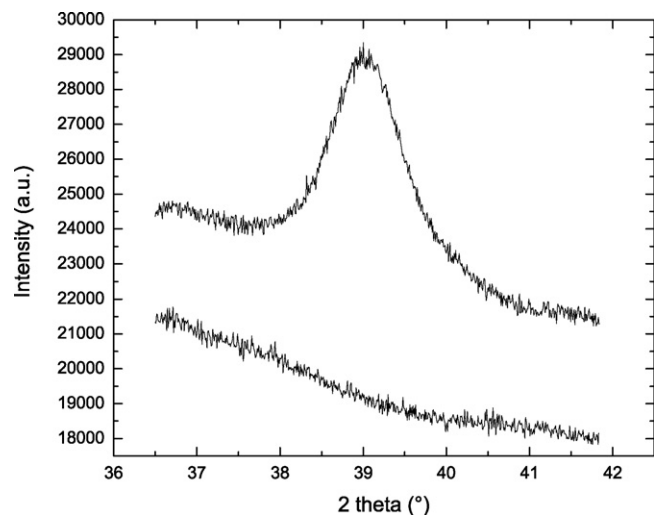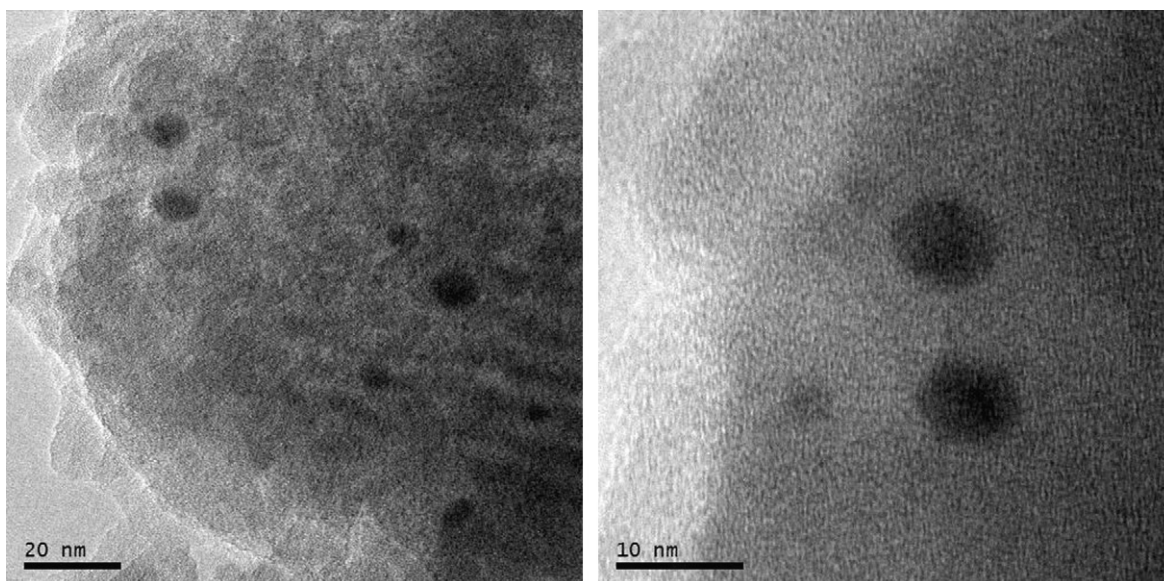

Fig. 5. HR TEM images of fresh catalyst **3**: a view of the representative area (left) and a detail of the metallic particles (right).
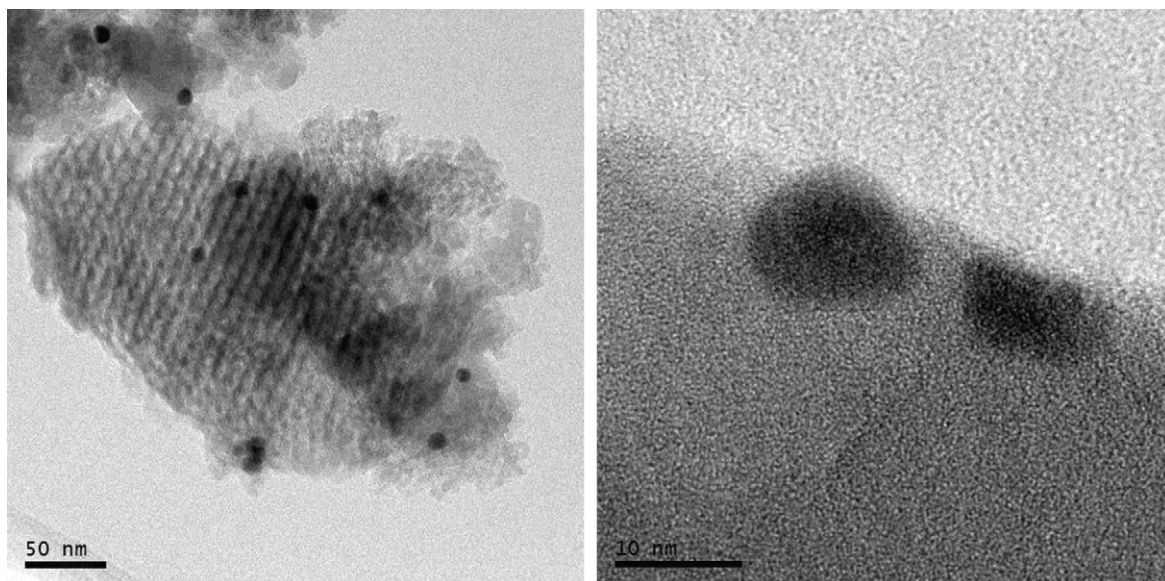
Fig. 6. HR TEM images of catalyst **3** recovered after conventional hydrothermal reaction: a view of the representative area (left) and a detail of the metallic particles (right).

acting probably as a source of active metal for the educts. When the amount of palladium in the system was reduced to a half (cf. entries 5 and 6 in Table 2), the catalytic activity dropped to about a half as well. Catalysts **7** and **8** showed a rapid increase in the amount of the coupling product followed by deactivation. In the case of catalyst **7**, this can be attributed to a deficiency of the active metal that is not supplied fast enough from the support to compete with relatively rapid deactivation (e.g., growth of metallic particles). On the other hand, the loss of the activity of **8** probably reflects massive leaching of the metal and its rapid deactivation (Table 3).

The aggregation of the metallic particles was evidenced by the comparison of the X-ray diffraction patterns recorded for catalyst **3** before and after the reaction under thermal conditions (Fig. 4). The fresh catalyst did not exhibit any detectable peak in the region of the (1 1 1) diffraction of palladium metal [17] but the recycled

one showed a broad diffraction peak, indicating an increase in the coherent diffraction volume and, hence, in the particles size.

The particle growth during the reaction was established also by HR TEM analysis. In the microscopic images of the fresh catalyst **3** (Fig. 5), there were seen only small spherical metallic particles ca. 5 nm in diameter, well dispersed in the support [18]. The same catalyst recovered from the reaction mixture treated under conventional heating (160 °C for 4 h) showed slightly larger particles (ca. 7–8 nm) yet well separated and distributed in the solid matrix (Fig. 6). By contrast, catalyst **3** recovered after MW treatment displayed large aggregates consisting of smaller spherical domains (Fig. 7). This observation is in line with our previous findings suggesting that the deactivation of the catalyst due to particle growth is faster under MW irradiation than under conventional heating [19]. In addition, the shape of the aggregates indicates that, in addition to the atom chopping mechanism [3,20], simple clus-
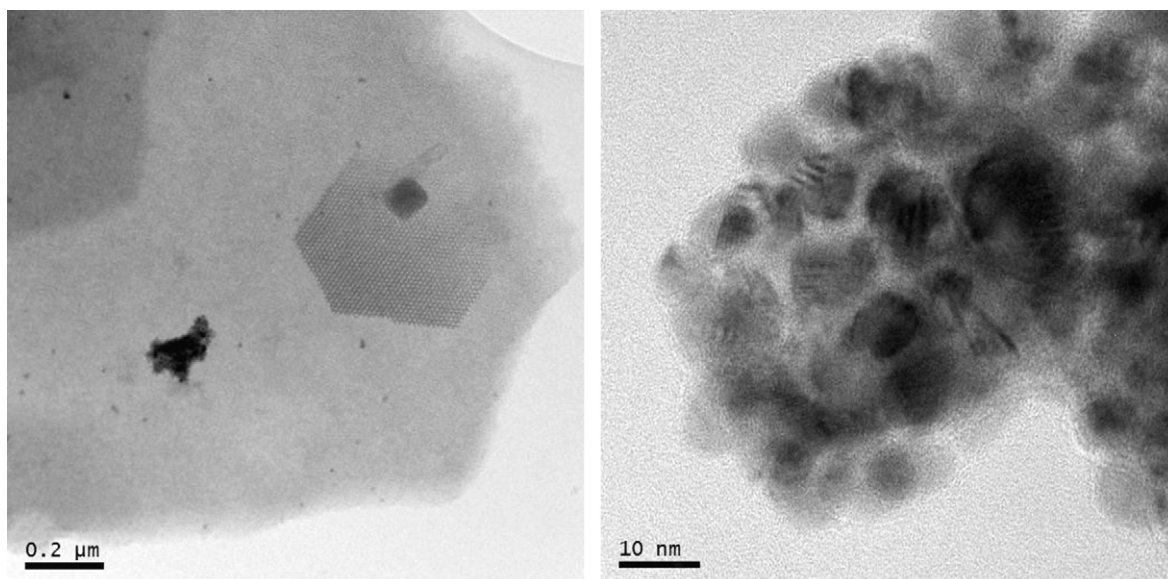

Fig. 7. HR TEM images of catalyst **3** recovered from a MW-treated reaction mixture: a general view (left) and a detailed view of the aggregated particles (right).

tering of metallic particles may also be involved in the particle growth.

3. Conclusions

In summary, the catalysts obtained by reacting mesoporous molecular sieves possessing N-donor groups at their surface with palladium(II) acetate catalyse the model Heck reaction both in a standard (with external base) or bifunctional manner under conventional thermal activation or microwave irradiation. It appears likely that the Pd-doped sieves serve as a reservoir of small palladium particles (atoms) that efficiently catalyse the coupling reaction and are (at least partially; see Table 3) re-deposited on the support [21]. The nature of the modifying N-groups seems to determine in large extent the activity of the formed catalyst through controlling, e.g., leaching of the metal component and catalyst deactivation.

The most efficient systems bearing the $\equiv$SiCH$_2$CH$_2$CH$_2$NH$_2$ (catalyst 3) and $\equiv$SiCH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$NEt$_2$ (catalyst 7) groups at their surface appear to be the best catalysts in the series studied, showing relatively low metal leaching and very good activities under both thermal and MW conditions that by far exceed those reported for systems based on unmodified MCM-41 and its ion-exchanged analogues [22] (Note: catalyst 8 gave a higher conversion under solvothermal conditions but suffered from extensive metal leaching). Additionally, catalyst 7 exerts the most pronounced bifunctional character, again surpassing the analogues featuring inorganic basic sites [8d,e,19,22]. As evidenced by HR TEM and by X-ray powder diffraction measurements, growth of the metallic particles is the main deactivation process, leading to a loss of activity upon repeated use.

4. Experimental

4.1. Materials and methods

Palladium(II) acetate (Aldrich), mesitylene (Fluka), bromobenzene (Aldrich), n-butyl acrylate (Aldrich), n-butyl cinnamate (Alfa Aesar), dry N,N-dimethylacetamide (Aldrich), diethylamine (Aldrich), poly(ethylene glycol)-block-poly(propylene glycol) block-poly(ethylene glycol) (Pluronic P123, (ethylene oxide)$_{20}$(propylene oxide)$_{70}$(ethylene oxide)$_{20}$; Aldrich), (3-aminopropyl) triethoxysilane (Aldrich), 3-chloropropyltriethoxysilane (Aldrich), 2-pyridinecarboxaldehyde (Aldrich), N,N,N-tris(2-aminoethyl)amine (Aldrich), 1,2-diaminoethane (Aldrich), and N-{2-(N,N-diethylamino)ethyl}amine (Aldrich) were used without further purification. Toluene was dried over molecular sieve 4 A. Sodium acetate was freshly melted before use to remove traces of water. All the catalysts were handled in air.

Nitrogen adsorption isotherms were measured on a Micromeritics ASAP 2020 volumetric instrument at −196 °C. Prior to the measurements the samples were carefully degassed at 130 °C until pressure of 10^{-3} Pa was attained (at least for 24 h). The textural parameters are summarised in Table 1. X-ray powder diffractograms were recorded with a Bruker D8 X-ray powder diffractometer equipped with a graphite monochromator and position-sensitive detector (Våntec–1) using Cu Kα radiation (λ = 1.5412 Å) and Bragg–Brentano arrangement (data acquisition details: low 2θ-region: 2θ = 0.5–10°, step 0.008536° at 0.5 s per step; high 2θ-region: 2θ = 36.5–41.8°, step 0.008536° at 25 s per step). FT IR spectra were recorded on a Nicolet Magna-IR AEM spectrometer using a cell connected to a vacuum apparatus (128 scans, 4 cm^{-1} resolution). Samples were pressed into self-supporting wafers with the density of ca. 10 mg cm^{-2}. Prior to the measurement, the samples were evacuated overnight in order to remove adsorbed water.

The palladium content was determined on an ICP-OES spectrometer (IRIS Intrepid II; Thermo Electron Corp.) equipped with an axial plasma and ultrasonic CETAC nebuliser, model U-5000AT+ (conditions: plasma power 1150 W, nebuliser pressure 25.0 psi, auxiliary gas flux 1.0 mL min^{-1}, sample uptake 2.4 mL min^{-1}). The samples were first dried at 100 °C for 3 h and then mineralised in a mixture of concentrated HF and HNO$_3$ (volume ratio 2/3; Suprapur Merck) at 50 °C for 15 min and diluted with re-distilled water. Analytical line 324.270 nm was used for Pd measurements. The content of carbon, hydrogen, nitrogen and chloride was determined by the standard combustion analysis.

High-resolution transmission electron micrographs were obtained on a Philips EM 201 instrument operating at 80 kV. Copper grid coated with a holey carbon support film was used to prepare the samples: the catalyst samples were dispersed in little ethanol, sonicated for 10 min and the carbon coated copper grid was dipped into this suspension.

Chloropropylated mesoporous molecular sieve (material 1) was prepared by direct synthesis under microwave irradiation as follows. Template tri-block copolymer P123 (10.0 g) and sodium silicate nonahydrate (27.35 g, 0.0962 mol) were dissolved in water (256 mL) by stirring at room temperature for several hours. Then, 35% HCl (67.5 mL, 0.78 mol) was added and the mixture vessel was immersed into a water bath kept at 50 °C. After 1 min, (3-chloropropyl)triethoxysilane (1.88 g, 7.8 mmol; this amount corresponds to 7.5% of all Si atoms in the reaction solution) was added, and the resulting mixture was stirred at 50 °C for 1 h and then put into microwave oven and heated to 100 °C for 3 h (see Ref. [13]). Characterisation data for material 1 are as follows: powder X-ray diffraction (2θ/°): 0.91 (s), 1.59 (m), 1.81 (m). Elemental analysis: C 9.7 mmol g^{-1}, Cl 0.80 mmol g^{-1}.

Aminopropylated mesoporous molecular sieve (material 2) was prepared by a procedure similar to the preparation of 1. Template tri-block copolymer P123 (10.0 g) and sodium silicate nonahydrate (27.35 g, 0.0962 mol) were dissolved in water (256 mL) by stirring at room temperature for several hours and the solution was treated with (3-aminopropyl)triethoxysilane (1.73 g, 7.8 mmol; this amount corresponds to 7.5% of all Si atoms in the mixture). The resulting mixture was transferred to a water bath maintained at 50 °C and, after 10 min, 35% HCl (67.5 mL, 0.78 mol) was added. The mixture was stirred at 50 °C for 1 h and then heated in a microwave oven to 100 °C for 2 h. For details, see Ref. [14]. Characterisation data for material 2 are as follows: IR (cm^{-1}): 3738 (s), 3374 (m), 3312 (m), 2979 (w), 2941 (s), 2874 (s), 1962 (w), 1862 (m), 1593 (s), 1449 (m), 1411 (m), 1392 (w). Powder X-ray diffraction (2θ/°): 0.81 (s), 1.3 (m), 1.6 (m), 2.1 (w).

4.2. Preparation of catalysts

4.2.1. Modification of material 1

Mixture of material 1 (1 g) and the corresponding amine (17 mmol) in toluene (30 mL) was stirred at 100 °C for 30 h under nitrogen (the reaction with diethylamine was performed at 60 °C due to the lower boiling point of this amine). The solid was filtered off, washed out with ethanol and dried. The resulting yellowish powder was stirred in mixture of 25% aqueous ammonia and ethanol (1:3, ca. 100 mL) for 3 h, the mixture was filtered, and the residue was washed with ethanol and dried in air at 80 °C. The resulting solid was directly used in the next step (i.e., for the reaction with palladium(II) acetate; see the following sections).

4.2.2. Preparation of catalyst 3

Material 2 (1 g) was added to a solution of palladium acetate (22.5 mg, 0.1 mmol) in dichloromethane (30 mL). The mixture was stirred for 1 h at room temperature and then filtered. The solid was

thoroughly washed with dichloromethane and dried in air at room temperature.

Characterisation: powder X-ray diffraction $(2\theta/°)$: 0.8 (s), 1.3 (m), 1.5 (m), 2.0 (w). Elemental analysis: Pd 0.110 mmol g^{-1}, C 4.4 mmol g^{-1}, N 0.72 mmol g^{-1}. IR (cm^{-1}): 3738 (s), 3307 (w), 2937 (m), 1977 (w), 1863 (m), scissoring NH$_2$ 1592 (s), 1561 (s), 1410 (s).

4.2.3. Preparation of catalyst 4

Catalyst **4** was prepared by deposition of palladium acetate onto solid support bearing the *N*-{2-[*N,N*-bis(2-aminoethyl) aminoethyl]}aminopropyl groups, as given above for catalyst **3**. Characterisation: elemental analysis: Pd 0.099 mmol g^{-1}, C 11.0 mmol g^{-1}, N 4.4 mmol g^{-1}, Cl 0.4 mmol g^{-1}. IR (cm^{-1}): 1848 (w), 1658 (s), 1597 (s), 1461 (s), 1410 (w), 1354 (m). IR of the parent, amine-modified material (cm^{-1}): 1846 (w), 1649 (s), 1597 (s), 1462 (s), 1409 (w), 1371 (m), 1354 (m).

4.2.4. Preparation of catalyst 5

Catalyst **5** was prepared by deposition of palladium acetate onto solid support containing *N*-[*N*-(2-aminoethyl)]aminopropyl groups, as given above for catalyst **3**. Characterisation: elemental analysis: Pd 0.103 mmol g^{-1}, C 6.6 mmol g^{-1}, N 1.8 mmol g^{-1}, Cl 0.0 mmol g^{-1}. IR (cm^{-1}): 1864 (w), 1656 (s), 1598 (s), 1562 (s), 1552 (s), 1462 (m), 1452 (m), 1412 (s), 1352 (w). IR of the parent, amine-modified material (cm^{-1}): 1968 (w), 1859 (m), 1657 (s), 1602 (s), 1499 (w), 1459 (m), 1412 (w), 1354 (m).

4.2.5. Preparation of catalyst 6

Catalyst **6** was prepared by deposition of palladium acetate onto solid support containing *N*-(*N,N*-diethyl)aminopropyl groups, as given above for catalyst **3**. Characterisation: elemental analysis: Pd 0.093 mmol g^{-1}, C 5.8 mmol g^{-1}, N 0.4 mmol g^{-1}, Cl 0.7 mmol g^{-1}. IR (cm^{-1}): 1973 (w), 1863 (m), 1711 (w), 1558 (s), 1473 (m), 1445 (m), 1412 (s). IR of the parent, amine-modified material (cm^{-1}): 1961 (w), 1863 (m), 1634 (m), 1474 (s), 1461 (s), 1447 (s), 1411 (s), 1396 (m), 1352 (s).

4.2.6. Preparation of catalyst 7

Catalyst **7** was prepared by deposition of palladium acetate onto solid support containing *N*-[2-(*N,N*-diethylamino) ethyl]aminopropyl groups, as given above for catalyst **3**. Characterisation: elemental analysis: Pd 0.101 mmol g^{-1}, C 8.6 mmol g^{-1}, N 1.6 mmol g^{-1}, Cl 0.1 mmol g^{-1}. IR (cm^{-1}): 1983 (w), 1861 (m), 1564 (s), 1470 (s), 1461 (s), 1409 (s), 1395 (s). IR of the parent, amine-modified material (cm^{-1}): 1955 (w), 1855 (m), 1646 (m), 1473 (s), 1472 (s), 1410 (w), 1391 (s), 1352 (m).

4.2.7. Preparation of catalyst 8

Pyridine-2-carboxaldehyde (0.749 g, 7 mmol) was added to a suspension of material **2** (1 g) in ethanol (100 mL). The reaction vessel was flushed with nitrogen and the mixture was stirred at room temperature for 17 h. Then, the solid part was filtered, washed with ethanol and dried at 80 °C on air. Subsequent deposition of palladium acetate was carried out as given above for catalyst **3**. Characterisation: elemental analysis: Pd 0.103 mmol g^{-1}, C 5.9 mmol g^{-1}, N 1.2 mmol g^{-1}. IR (cm^{-1}): 3736 (s), 3292 (w), 2937 (s), 1971 (w), 1863 (m), 1722 (m), 1597 (s), 1566 (s), 1550 (s), 1477 (m), 1440 (m), 1412 (s). IR of the parent, N-modified material (cm^{-1}): 1955 (w), 1855 (m), 1646 (m), 1473 (s), 1472 (s), 1410 (w), 1391 (s), 1352 (m).

4.3. Catalytic tests

Catalytic tests under microwave irradiation were performed in a microwave oven CEM Discover in a 50 mL round flask equipped with a condenser. Hydrothermal catalytic experiments were carried out with a Heidolph Synthesis I (system of 16-parallel reactions). The reaction mixture consisted of *n*-butyl acrylate (64 mg, 0.5 mmol), bromobenzene (118 mg, 0.75 mmol), sodium acetate (63 mg, 0.75 mmol) if appropriate, mesitylene (50 mg, 0.42 mmol), DMA (2.5 mL) and 50 mg of catalyst (1 mol% Pd with respect to *n*-butyl acrylate). The reaction mixture was thoroughly flushed with nitrogen prior to the reaction. Reactions performed under microwave irradiation were carried out at the temperature 165 °C (boiling point of DMA) with continuous microwave power 300 W. Reactions under conventional hydrothermal conditions were performed at 160 °C.

The progress of the reaction was monitored by taking samples that were subsequently centrifuged at 4000 rpm and analysed by a high-resolution gas chromatography (Agilent 6890 chromatograph equipped with a flame ionisation detector and HP-1 column or Agilent 6850 chromatograph equipped with a flame ionisation detector and HP-5). The identity of the reaction product was checked by GC–MS (Agilent 5975).

References

[1] (a) S. Bräse, A. de Meijere, in: F. Diederich, P.J. Stang (Eds.), Metal-Catalyzed Cross-Coupling Reactions, Wiley–VCH, New York, 1998, pp. 99–166;
(b) S. Bräse, A. de Meijere, in: A. de Meijere, F. Diederich (Eds.), Metal-Catalyzed Cross-Coupling Reactions, 2nd ed., Wiley–VCH, Weinheim, 2004, pp. 217–315.
[2] (a) R.F. Heck, J.P. Nolley, J. Org. Chem. 37 (1972) 2320;
(b) T. Mizoroki, K. Mori, A. Ozaki, Bull. Chem. Soc. Jpn. 44 (1971) 581.
[3] For a recent introductory review, see: D. Astruc, Inorg. Chem. 46 (2007) 1884.
[4] (a) T. Jeffery, Chem. Commun. (1984) 1287;
(b) I. Pryjomska-Ray, A.M. Trzeciak, J.J. Ziółkowski, J. Mol. Catal. A: Chem. 257 (2006) 3;
(c) M.T. Reetz, J.G. de Vries, Chem. Commun. (2004) 1559.
[5] M.T. Reetz, G. Lohmer, Chem. Commun. (1996) 1921.
[6] (a) S. Chandrasekhar, C. Narsihmulu, S.S. Sultana, N.R. Reddy, Org. Lett. 4 (2002) 4399;
(b) A. Gniewek, A.M. Trzeciak, J.J. Ziółkowski, L. Kępiński, J. Wrzyszcz, W. Tylus, J. Catal. 229 (2005) 332;
(c) A. Corma, H. García, A. Leyva, J. Catal. 240 (2006) 87;
(d) M.A.R. Meier, M. Filali, J.-F. Gohy, U.S. Schubert, J. Mater. Chem. 16 (2006) 3001;
(e) I.P. Beletskaya, A.N. Kashin, A.E. Litvinov, V.S. Tyurin, P.M. Valetsky, G. van Koten, Organometallics 25 (2006) 154;
(f) P. Ribière, V. Declerck, Y. Nédellec, N. Yadav-Bhatnagar, J. Martinez, F. Lamaty, Tetrahedron 62 (2006) 10456.
[7] R.W.J. Scott, O.M. Wilson, R.M. Crooks, J. Phys. Chem. B 109 (2005) 692.
[8] (a) R.L. Augustine, S.T. O'Leary, J. Mol. Catal. A: Chem. 95 (1995) 277;
(b) C.P. Mehnert, D.W. Weaver, J.Y. Ying, J. Am. Chem. Soc. 120 (1998) 12289;
(c) A. Corma, H. García, A. Leyva, Appl. Catal. A 236 (2002) 179;
(d) A. Corma, H. García, A. Leyva, A. Primo, Appl. Catal. A 247 (2003) 41;
(e) A. Corma, H. García, A. Leyva, A. Primo, Appl. Catal. A 257 (2004) 77;
(f) A. Papp, G. Galbács, Á. Molnár, Tetrahedron Lett. 46 (2005) 7725;
(g) L. Li, J. Shi, J. Yan, Chem. Commun. (2004) 1990;
(h) A. Corma, H. Garcia, A. Leyva, J. Mol. Catal. A: Chem. 230 (2005) 97.
[9] (a) J.S. Beck, J.C. Vartuli, J.W. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834;
(b) A. Taguchi, F. Schüth, Micropor. Mesopor. Mater. 77 (2005) 1.
[10] For selected examples of alternative approaches that making use of other anchoring groups, see:
(a) Q. Hu, J.E. Hampsey, N. Jiang, C. Li, Y. Lu, Chem. Mater. 17 (2005) 1561;
(b) C.M. Crudden, M. Sateesh, R. Lewis, J. Am. Chem. Soc. 127 (2005) 10045;
(c) Q. Xu, W. Hao, M. Cai, Catal. Lett. 118 (2007) 98;
(d) J.D. Webb, S. MacQuarrie, K. McEleney, C.M. Crudden, J. Catal. 252 (2007) 97;
(e) C.M. Crudden, K. McEleney, S.L. MacQuarrie, A. Blanc, M. Sateesh, J.D. Webb, Pure Appl. Chem. 79 (2007) 247;
(f) K. Shimizu, S. Koizumi, T. Hatamachi, H. Yoshida, S. Komai, T. Kodama, Y. Kitayama, J. Catal. 288 (2004) 141;

(g) E. Paetzold, G. Oehme, H. Fuhrmann, M. Richter, R. Eckelt, M.-M. Pohl, H. Kosslick, Micropor. Mesopor. Mater. 44–45 (2001) 517;
(h) H. Kosslick, I. Mönnich, E. Paetzold, H. Fuhrmann, R. Fricke, D. Müller, G. Oehme, Micropor. Mesopor. Mater. 44–45 (2001) 537.

[11] (a) J. Horniakova, T. Raja, Y. Kubota, Y. Sugi, J. Mol. Catal. A: Chem. 217 (2004) 73;
(b) J.H. Clark, D.J. Macquarrie, E.B. Mobofu, Green Chem. 2 (2000) 53;
(c) E.B. Mubofu, J.H. Clark, D.J. Macquarrie, Green Chem. 3 (2001) 23;
(d) S. Paul, J.H. Clark, J. Mol. Catal. A: Chem. 215 (2004) 107;
(e) M. Lagasi, P. Moggi, J. Mol. Catal. A: Chem. 182–183 (2002) 61;
(f) C. González-Arellano, A. Corma, M. Iglesias, F. Sánchez, Adv. Synth. Catal. 346 (2004 1758);
(g) D.J. Macquarrie, B. Gotov, Š. Toma, Platinum Met. Rev. 45 (2001) 102.

[12] (a) P. Yi, Z. Zhuangyu, H. Hongwen, J. Mol. Catal. 62 (1990) 297;
(b) J. Zhou, R. Zhou, L. Mo, S. Zhao, X. Zheng, J. Mol. Catal. A: Chem. 178 (2002) 289;
(c) S. Mandal, D. Roy, R.V. Chaudhari, M. Sastry, Chem. Mater. 16 (2004) 3714;
(d) S.F. Zhao, R.X. Zhou, X.M. Zheng, J. Mol. Catal. A: Chem. 211 (2004) 139;
(e) O. Vassylyev, J. Chen, A.P. Panarello, J.G. Khinast, Tetrahedron Lett. 46 (2005) 6865;
(f) V. Polshettiwar, P. Hesemann, J.J.E. Moreau, Tetrahedron 63 (2007) 6784;
(g) H. Li, L. Wang, P. Li, Synthesis (2007) 1635.

[13] Sujandi, S.-E. Park, Stud. Surf. Sci. Catal. 170 (2007) 1446.

[14] Sujandi, S.-E. Park, D.-S. Han, S.-C. Han, M.-J. Jin, T. Ohsuna, Chem. Commun. (2006) 4131.

[15] Interpretations based on elemental analysis of samples showing low chlorine contents should be taken with care due to relatively large uncertainity of experimental values close to the detection limit.

[16] There was no coupling product detected in the reactions performed (solvothermal reactions for 4 h) in the presence of material **1** or the precursor sieve to catalyst **7** (i.e., with the respective amine-modified sieve containing no palladium).

[17] PDF card 5-0681: palladium, cubic, space group *Fm–3m* (no. 225), $a = 3.8898$ Å at 26 °C; *hkl* 1 1 1, $d = 2.246$ Å, relative intensity = 100, $2\theta \approx 40°$ at Cu Kα.

[18] It should be noted, however, that TEM is not fully reliable in this case as the electron beam may induce formation of metallic particles:
(a) J.D. Aiken III, R.G. Finke, J. Mol. Catal. A: Chem. 145 (1999) 1;
(b) G. Schmid, Chem. Rev. 92 (1992) 1709;
(c) C.M. Hagen, L. Vieille-Petit, G. Laurenczy, G. Süss-Fink, R.G. Finke, Organometallics 24 (2005) 1819;
(d) C.M. Hagen, J.A. Widegren, P.M. Maitlis, R.G. Finke, J. Am. Chem. Soc. 127 (2005) 4423;
(e) C.A. Jaska, I. Manners, J. Am. Chem. Soc. 126 (2004) 1334;
(f) C.A. Jaska, I. Manners, J. Am. Chem. Soc. 126 (2004) 9776.

[19] J. Demel, S.-E. Park, J. Čejka, P. Štěpnička, Catal. Today 132 (2008) 63.

[20] M.B. Thathagar, J.E. ten Elshof, G. Rothenberg, Angew. Chem. Int. Ed. 45 (2006) 2886.

[21] See Ref. [3] and references cited therein.

[22] J. Demel, J. Čejka, P. Štěpnička, J. Mol. Catal. A: Chem. 274 (2007) 127.