Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 132 (2008) 63–67
CATALYSIS TODAY
www.elsevier.com/locate/cattod

The use of palladium nanoparticles supported with MCM-41 and basic (Al)MCM-41 mesoporous sieves in microwave-assisted Heck reaction

Jan Demel [a,b], Sang-Eon Park [c], Jiří Čejka [b], Petr Štěpnička [a,*]

[a] Charles University in Prague, Faculty of Science, Department of Inorganic Chemistry, Hlavova 2030, 12840 Prague 2, Czech Republic
[b] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i, Dolejškova 3, 18223 Prague 8, Czech Republic
[c] Laboratory of Nano-Green Catalysis, Nano Center for Fine Chemicals Fusion Technology, Department of Chemistry, Inha University, Incheon 402-751, Republic of Korea

Abstract

A series of supported catalysts has been obtained by grafting of chemically generated palladium nanoparticles onto basic, Cs^+ ion-exchanged molecular sieves (Al)MCM-41 and onto the non-basic, parent material MCM-41. Catalytic activity of the catalysts has been investigated in the Heck reaction between bromobenzene and butyl acrylate under microwave irradiation. The activity of the bifunctional catalysts (Pd@Cs^+-(Al)MCM-41) and the activity of Pd@MCM-41 combined with sodium acetate as an external base were considerably higher under microwave irradiation than activities observed for the same catalytic systems under the conventional heating. The Pd@MCM-41/NaOAc system showed higher conversions than the bifunctional catalysts presumably due to a different nature and accessible amount of the base. On the other hand, microwave irradiation seems to increase the rate of aggregation of the metallic particles and thus also catalyst deactivation as compared with the usual heating.

Keywords: Bifunctional catalysts; Supported catalysts; Palladium; Nanoparticles; MCM-41; Heck reaction; Microwaves

1. Introduction

Carbon–carbon and carbon–heteroatom bond-forming reactions represent an indispensable tool for organic synthesis, finding numerous applications in the preparation of fine chemicals. One of the most frequently utilised palladium-catalysed C–C coupling reactions is the Heck reaction that affords substituted alkenes from aryl halides and activated alkenes [1]. In recent years, great effort has been devoted to the development of catalytic systems for Heck reaction that are capable of activating relatively cheaper but much less reactive aryl chlorides and also to catalysts that could be used repeatedly [2]. Recently, the later approach led to the design of active supported catalysts [3].

Microwave irradiation has found a widespread application in inorganic and organic synthesis, being more energy efficient and usually inducing higher reaction rates in comparison with the conventional conditions. As opposed to the usual thermal treatment, where the heat (energy) is distributed by conductive way, microwaves are absorbed directly by polar components of the reaction mixture and, hence, the energy is delivered directly to the reacting partners [4].

In 1996, Hallberg and co-workers applied microwave irradiation to Heck reaction [5]. Since then a wide range of reactants, solvents and bases have been studied [6]. Heck reactions performed under microwave irradiation typically proceed with similar overall yields and regioselectivity but with notably shorter reaction times as compared to the standard thermal activation. This acceleration of the reaction rates is probably caused by a rapid *in situ* heating or the so-called superheating effect [6g].

Bifunctional catalysts obtained by Corma and co-workers by impregnation of basic, ion-exchanged zeolites and sepiolite with palladium(II) chloride exhibited relatively low activity in Heck reaction, requiring very high catalyst loading for the reaction to proceed satisfactorily [3e,f]. In our previous work we have prepared bifunctional catalysts via combining palladium nanoparticles as the catalytically active centres with

* Corresponding author.
E-mail address: stepnic@natur.cuni.cz (P. Štěpnička).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.12.007

basic solid supports – Cs^+ ion-exchanged aluminium-containing mesoporous molecular sieves – and studied them as catalysts for Heck coupling of *n*-butyl acrylate with bromobenzene under conventional heating [7]. Herein we report the utilisation of these catalysts in microwave-promoted Heck reaction.

2. Results and discussion

2.1. Preparation and characterisation of the catalysts

The supported catalysts have been obtained by grafting of chemically generated palladium nanoparticles onto selected solid supports and characterised as previously reported [7]. The nanoparticles were generated by reduction of palladium(II) acetate in dry THF in the presence tetrabutylammonium acetate at reflux temperature [8]. Since the nanoparticles spontaneously deposited upon addition of the solid support to the reaction mixture, the supported catalysts were isolated by simple filtration. The solid materials were washed with diethyl ether and shortly dried in the air to not evaporate completely the polar solvent, which seems to stabilise the metallic particles [8b].

To investigate the role of the support on the course of the catalysed reaction, we chose the following materials for deposition of the nanoparticles: in-synthesis Al-doped mesoporous molecular sieve MCM-41 ((Al)MCM-41), which has been ion-exchanged with cesium ions (Cs^+-(Al)MCM-41 to give catalyst 1) and the same material calcined at 450 °C for 4 h prior to the deposition of the metal nanoparticles (calcined Cs^+-(Al)MCM-41 to give catalyst 2). For a comparison, we also included the inherently basic zeolite Y after ion-exchange (Cs^+-zeolite Y to give catalyst 3) as well as all-siliceous MCM-41 as the non-basic support (catalyst 4). Thus, whereas catalysts 1–3 already contain basic sites (i.e., they are bifunctional), their non-basic counterpart 4 requires the presence of an external base.

The catalysts were characterised in the usual manner, i.e. by elemental analysis, X-ray powder diffraction and by nitrogen adsorption isotherms. All materials showed the palladium content of around 0.08 mmol g^{-1}. By contrast, the amount of cesium ions (or the base) differed: the (Al)MCM-41 based catalysts (1 and 2) had Cs^+ content slightly below 0.05 mmol g^{-1} while catalyst 3 supported with the more basic zeolite Y exerted Cs^+ content almost five times higher (0.22 mmol g^{-1}).

X-ray powder diffraction patterns for all the MCM-41-based nanoparticle catalysts 1 and 2 were very similar, showing four characteristic diffraction lines in the region of $2\theta < 10°$, which indicates the hexagonal structure of the supports to be unaffected by deposition of the metal particles [9]. Even so, the nitrogen adsorption isotherms of catalysts 1 and 2 displayed an increase in the adsorbed amount of nitrogen at p/p_0 of about 0.3–0.4 as it is typical for hexagonal mesoporous molecular sieves with cylindrical pores of narrow pore size distribution [9]. Fig. 1 shows typical adsorption isotherms for catalyst 2 and its parent (Al)MCM-41; the calculated textural parameters are given in Section 4.

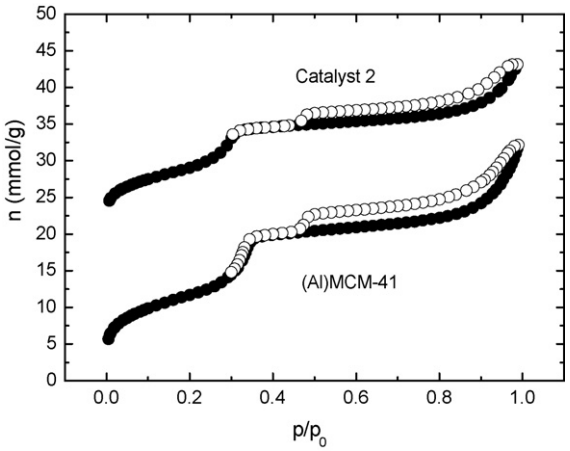

Fig. 1. Nitrogen adsorption isotherms for catalyst 2 and it parent support, (Al)MCM-41. For clarity, the isotherm for catalyst 2 is shifted along the *y*-axis by +20 mmol g^{-1}.

2.2. Catalytic experiments

The catalytic activity of the supported bifunctional catalysts 1–3 and their non-basic analogue 4 has been assessed in the Heck reaction between bromobenzene and *n*-butyl acrylate to give butyl cinnamate (Scheme 1) under continuous microwave irradiation using catalyst amount corresponding to 1 mol% of palladium and *N*,*N*-dimethylacetamide (DMA) as the solvent. For catalyst 4, anhydrous sodium acetate was added as the base.

Kinetic profiles presented in Fig. 2 together with the numerical data in Table 1 indicate that the Pd-nanoparticle bifunctional catalysts 1 and 2 supported with basic, Cs^+-exchanged (Al)MCM-41 are active in promoting Heck reaction under microwave irradiation, showing turnover numbers (TON) 11 and 30 after 10 h of the reaction [10], respectively. Such conversions and reaction rates are markedly higher as compared with those obtained for the same reaction and catalyst under conventional conditions (in DMA at 160 °C: TON = 8.0; TOF = 0.4 h^{-1}) [7].

The higher activity of the catalyst based on Cs^+-(Al)MCM-41 support that has been calcined before the deposition of the metal component (catalyst 2) can be attributed to thermally induced removal of anions (NO_3^-) from the solid matrix and, thus, an increased basicity of the support. This assumption is supported by comparable activities of catalyst 2 and zeolite Y-based catalyst 3, which contains more basic sites, though the conversion is not proportional to the Cs^+-content. The activity of catalyst 2 increased only slightly after addition of sodium acetate (TON = 35; TOF = 3.5 h^{-1}). On the other hand, catalyst

Scheme 1.

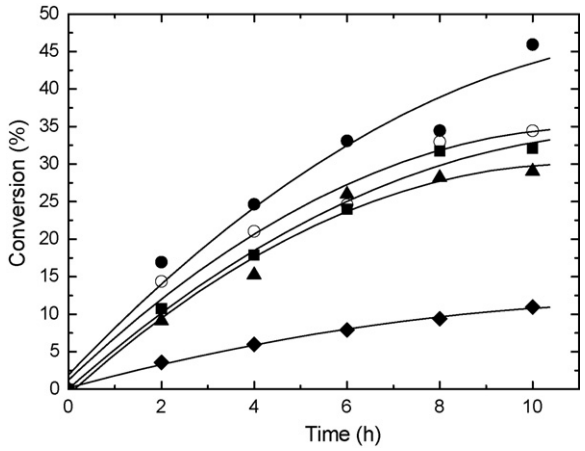

Fig. 2. Kinetic profiles for reactions performed in the presence of: catalyst 1 (◆), catalyst 2 (▲), catalyst 2 combined with external base (NaOAc) (○), catalyst 3 (■) and catalyst 4 combined with NaOAc (●). The numerical values are given in Table 1.

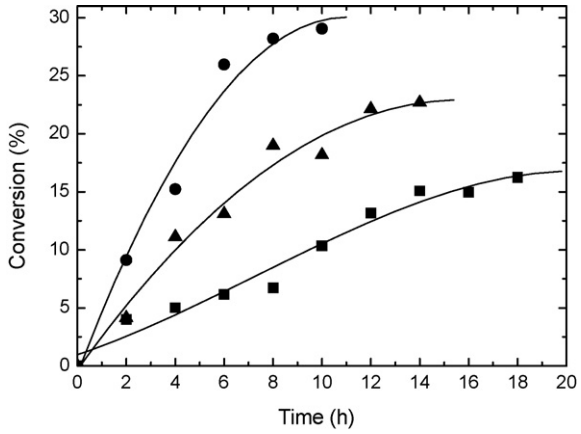

Fig. 3. Pd@(Al)MCM-41 calcined after ion exchange in three amounts in reaction mixture, 1 mol% (●), 0.75 mol% (▲) and 0.5 mol% (■).

4 combined with sodium acetate showed by far the best conversions (TON = 44; TOF = 4.4 h^{-1}). Clearly, the available amount and nature of the base (basic centres) are decisive for the catalyst activity of the tested nanoparticle catalysts. This can be demonstrated by a series of experiments, in which varying amounts of catalyst 2 were added to the reaction mixture (Fig. 3). In the tested series with 0.5, 0.75 and 1.0 mol% Pd, the maximum obtained conversions increased with the amount of catalyst, being directly proportional to the amount of catalyst. This observation can be accounted for by the loss of catalytic activity when the accessible base is consumed and/or by catalyst deactivation.

In order to determine the catalyst stability under microwave irradiation we have performed leaching and recycling tests and also investigated particle aggregation by means of X-ray powder diffraction analysis. In one experiment, catalyst 2 has been recovered from the cold reaction mixture after 10 h of the reaction, rinsed thoroughly with ethanol and acetone, calcined at 400 °C for 5 h, and then used again under otherwise identical reaction conditions. Such recycled bifunctional catalyst showed only 5% conversion after 10 h, which is about one sixth of the conversion observed with the fresh one (29%).

In another experiment, possible leaching of the active metal species has been studied by means of removal of the catalyst from the reaction mixture by centrifugation of the reaction mixture and filtering through a 0.45 μm PTFE syringe microfilter. Although the reaction rate markedly decreased, the reaction did not stop immediately but rather gradually slowed down (Fig. 4). Since it was proven that leaching of the active species occurs during Heck reaction catalysed with palladium nanoparticles [11], plausible explanation of the observed kinetic profile is that some active species remain available in the reaction solution even shortly after the removal of the bulk catalyst but they loose catalytic activity upon further heating to the reaction temperature.

A more detailed analysis of the behaviour of palladium particles during the catalytic run was performed using powder X-ray diffraction. The particle growth was established by an inspection of the region of palladium (1 1 1) diffraction [12]. Fig. 5 shows that whereas fresh catalyst 2 displays no detectable diffraction line attributable to bulk palladium, the same material recovered from the reaction mixture after 10 h of the reaction shows clearly discernible broad peak. A simple comparison with X-ray diffraction patterns obtained for the same material used under conventional heating [7] revealed that

Table 1
Summary of catalytic results[a]

Catalyst	Conversion (%)	TON
1	11	11
2	30	30
2[b]	35	35
3	33	33
4[b]	44	44

[a] In DMA at reflux temperature after 10 h. See experimental for details.
[b] Combined with NaOAc as an external base.

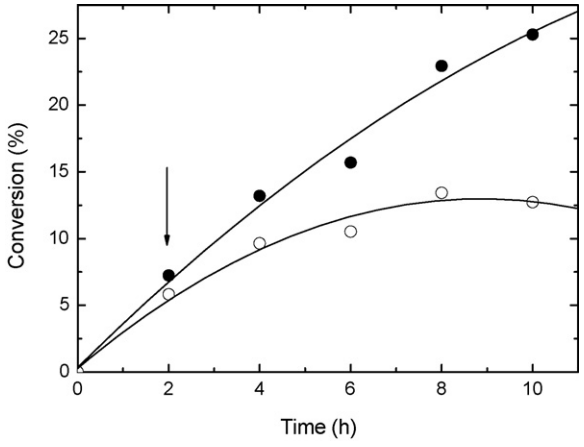

Fig. 4. A comparison of a normal catalytic run with catalyst 2 (●) with the same system from which the solid catalyst was removed after 2 h of reaction (○). The removal time is indicated by an arrow.

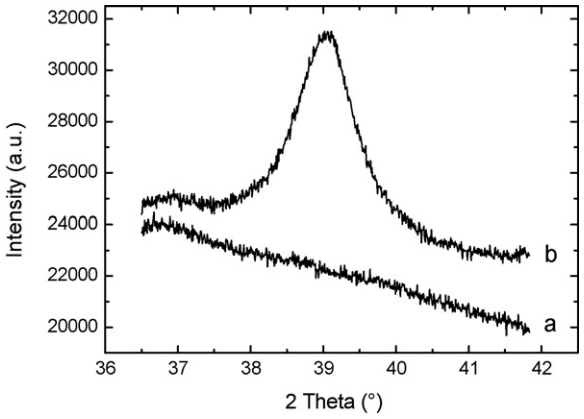

Fig. 5. Powder X-ray diffraction patterns obtained for fresh catalyst 2 (a) and the same material recovered after 10 h of the reaction time under microwave irradiation (b). The curves are shifted along the *y*-axis to avoid overlaps.

the aggregation is more pronounced under microwave irradiation than under conventional heating. This observation is in line with the different nature of thermal activation (convection vs. directed *in situ* heating).

3. Conclusions

Catalytic activities of palladium nanoparticles supported with basic molecular sieves (bifunctional catalysts) and with MCM-41 when combined with an external base are about ten times higher under microwave irradiation than similar systems under normal thermal activation [7]. However, microwave irradiation increases the rate of aggregation of the metallic particles leading to a faster catalyst deactivation.

4. Experimental

4.1. Materials

All siliceous MCM-41 and (Al)MCM-41 were prepared by similar procedures, differing only by the presence or absence of sodium aluminate in the reaction mixture. In the preparation of (Al)MCM-41, hexadecyltrimethylammonium bromide (9.80 g, Fluka), sodium aluminate (0.32 g, Riedel de Haen) and sodium metasilicate (10.0 g, Riedel de Haen) were dissolved in distilled water (950 mL; Si/Al molar ratio = 21). Ethyl acetate (15 mL, Fluka) was added to the solution and the resulting mixture was thoroughly mixed, allowed to age at room temperature for 5 h and, finally, heated at 90 °C for 60 h. The formed solid was filtered off while warm, washed well with water, dried and calcined at 550 °C for 6 h. MCM-41 was obtained in an analogous manner but without added sodium aluminate [13].

Zeolite Y (Slovnaft VÚRUP, Slovakia; Si/Al molar ratio 2.2), palladium(II) acetate (Aldrich), tetrabutylammonium acetate (Fluka), mesitylene (Aldrich), bromobenzene (Aldrich), *n*-butyl acrylate (Aldrich), *n*-butyl cinnamate (Alfa Aesar) and dry *N*,*N*-dimethylacetamide (Aldrich) were used without further purification. Sodium acetate was freshly melted before use in order to remove traces of water. The catalysts were handled in air.

4.2. Methods

Nitrogen adsorption isotherms were measured on a Micromeritics ASAP 2020 volumetric instrument at −196 °C. Prior to the measurements the samples were degassed at 250 °C until pressure of 10^{-3} Pa was attained (at least for 24 h). X-ray powder diffractograms were recorded on 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 (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).

The content of palladium and cesium was determined on an ICP-OES spectrometer (IRIS Intrepid II; Thermo Electron Corp.) equipped with 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 2.40 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. Due to technical limitation of the detector, Cs content was quantified on a less sensitive line at 184.254 nm.

4.3. Preparation of catalysts

4.3.1. Preparation of catalyst 1

(Al)MCM-41 was ion-exchanged with cesium cations by stirring four times with 0.5 M aqueous $CsNO_3$ solution (100 mL per 1 g of the sieve) at room temperature for 4 h. The slurry was filtered and the solid thoroughly washed with deionised water and dried at 90 °C. The resulting ion exchanged mesoporous sieve (1.00 g) was modified by palladium nanoparticles by refluxing with palladium acetate (0.1 mmol) and tetrabutylammonium acetate (0.315 mmol) in dry THF under argon atmosphere for 4 h as previously described [8].

Characterisation: powder X-ray diffraction: 2θ (°) 2.27 (s), 3.95 (w), 4.52 (vw), 6.00 (vw). Textural properties N_2-adsorption isotherms: BET surface area 818 $m^2 g^{-1}$, pore diameter 4.0 nm, pore volume 0.453 $cm^3 g^{-1}$. Elemental analysis: Pd 0.082 mmol g^{-1}, Cs 0.047 mmol g^{-1}.

4.3.2. Preparation of catalyst 2

(Al)MCM-41 was cesium ion-exchanged similarly to the support for catalyst 1 and then calcined at 450 °C for 4 h with a temperature increase 1 °C min^{-1}. The resulting powder was palladium-modified as described above for catalyst 1.

Characterisation: powder X-ray diffraction: 2θ (°) 2.25 (s), 3.86 (w), 4.47 (vw), 5.96 (vw). Textural properties N_2-adsorption isotherms: BET surface area 747 $m^2 g^{-1}$; pore diameter 3.9 nm; pore volume 0.419 $cm^3 g^{-1}$. Elemental analysis: Pd 0.081 mmol g^{-1}; Cs 0.049 mmol g^{-1}.

4.3.3. Preparation of catalyst 3

Catalyst 3 was prepared as given in detail for catalyst 1, starting from zeolite Y. Characterisation: elemental analysis: Pd 0.077 mmol g^{-1}, Cs 0.222 mmol g^{-1}.

4.3.4. Preparation of catalyst 4

Catalyst 4 was prepared by deposition of Pd nanoparticles onto all siliceous MCM-41 as given above for catalyst 1. Characterisation: powder X-ray diffraction: 2θ (°) 2.29 (s), 3.86 (w), 4.43 (vw), 5.83 (vw). Textural properties from N_2-adsorption isotherms: BET surface area 897 $m^2\,g^{-1}$; pore diameter 4.0 nm; pore volume 0.660 $cm^3\,g^{-1}$. Elemental analysis: Pd 0.070 mmol g^{-1}.

4.4. Catalytic tests

Catalytic tests were performed in a microwave oven CEM Discover in 50 mL round flask equipped with a condenser. The reaction mixture consisted of *n*-butyl acrylate (128 mg, 1.0 mmol), bromobenzene (236 mg, 1.5 mmol), sodium acetate (1.5 mmol) if appropriate, mesitylene (100 mg, 0.83 mmol), DMA (5 mL) and catalyst in an amount corresponding to 0.01 mmol of palladium (1 mol% with respect to *n*-butyl acrylate). The reactions were carried out at the temperature 165 °C (boiling point of DMA) with continuous microwave power 300 W.

The reaction was monitored by taking samples every 2 h, 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). The identity of the reaction product was checked by GC–MS (Agilent 5975). In the leaching test the reaction mixture was centrifuged after 2 h of the reaction. The supernatant was then filtered through PTFE microfilter (pore size 0.45 μm) and again heated in microwave oven. For recycling experiments the catalysts were recovered from the reaction mixture by filtration, thoroughly washed with ethanol and acetone, dried in air and calcined at 400 °C for 4 h.

References

[1] (a) S. Brase, A. de Meijere, in: F. Diederich, P.J. Stang (Eds.), Metal-catalyzed Cross-coupling Reactions, Wiley–VCH, New York, 1998, pp. 99–166;
(b) L. Yin, J. Liebscher, Chem. Rev. 107 (2007) 133;
(c) I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009;
(d) A.B. Dounay, L.E. Overman, Chem. Rev. 103 (2003) 2945.

[2] (a) V. Farina, Adv. Synth. Catal. 346 (2004) 1553;
(b) N.T.S. Phan, M. Van Der Sluys, C.W. Jones, Adv. Synth. Catal. 348 (2006) 609.

[3] (a) A. Biffis, M. Zecca, M. Basato, J. Mol. Catal. A: Chem. 173 (2001) 249;
(b) R.L. Augustine, S.T. O'Leary, J. Mol. Catal. A: Chem. 95 (1995) 277;
(c) C.P. Mehnert, D.W. Weaver, J.Y. Ying, J. Am. Chem. Soc. 120 (1998) 12289;
(d) A. Corma, H. García, A. Leyva, Appl. Catal. A. 236 (2002) 179;
(e) A. Corma, H. García, A. Leyva, A. Primo, Appl. Catal. A. 247 (2003) 41;
(f) A. Corma, H. García, A. Leyva, A. Primo, Appl. Catal. A 257 (2004) 77;
(g) L. Djakovitch, P. Rollet, Tetrahedron Lett. 45 (2004) 1367;
(h) L. Li, J. Shi, J. Yan, Chem. Commun. (2004) 1990;
(i) A. Corma, H. Garcia, A. Leyva, J. Mol. Catal. A: Chem. 230 (2005) 97.

[4] (a) A. Loupy (Ed.), Microwaves in Organic Synthesis, Wiley–VCH, Weinheim, 2002;
(b) A. Loupy (Ed.), Microwaves in Organic Synthesis, 2nd ed., Wiley, Weinheim, 2006;
(c) C.S. Cundy, Collect. Czech. Chem. Commun. 63 (1998) 1699.

[5] M. Larhed, A. Hallberg, J. Org. Chem. 61 (1996) 9582.

[6] (a) X. Xie, J. Lu, B. Chen, J. Hun, X. She, X. Pan, Tetrahedron Lett. 45 (2004) 809;
(b) G. Shoe, L. Morin, M.G. Organ, Angew. Chem. Int. Ed. 45 (2006) 2761;
(c) R.K. Arvela, N.E. Leadbeater, J. Org. Chem. 70 (2005) 1786;
(d) A. Stadler, B.H. Yousefi, D. Dallinger, P. Walla, E. Van der Eycken, N. Kaval, C.O. Kappe, Org. Process. Res. Dev. 7 (2003) 707;
(e) K.S.A. Valin, P. Emilsson, M. Larhed, A. Hallberg, J. Org. Chem. 67 (2002) 6243;
(f) D. Villemin, F. Caillot, Tetrahedron Lett. 42 (2001) 639;
(g) K.S.A. Ballin, M. Larged, K. Johansson, A. Hallberg, J. Org. Chem. 65 (2000) 4537.

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

[8] (a) M.T. Reetz, J.G. de Vries, Chem. Commun. (2004) 1559;
(b) J. Demel, J. Čejka, S. Bakardjieva, P. Štěpnička, J. Mol. Catal. A: Chem. 263 (2007) 259.

[9] J.S. Beck, J.C. Vartuli, W.J. 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.

[10] TON = mmol of product/mmol of Pd after 10 h of the reaction, TOF = -TON/reaction time.

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

[12] PDF card 5-0681: palladium, cubic, space group *Fm-3m* (no. 225), a = 3.8898 Å at 26 °C; *h k l* 111, 2.246 Å, rel. int. 100, $2\theta \approx 40^\circ$ at Cu Kα.

[13] J. Čejka, A. Krejčí, N. Žilková, J. Dědeček, J. Hanika, Microporous Mesoporous Mater. 44/45 (2001) 499.