

The use of palladium nanoparticles supported on MCM-41 mesoporous molecular sieves in Heck reaction: A comparison of basic and neutral supports

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Abstract

Bifunctional supported catalysts were prepared by grafting of chemically reduced palladium nanoparticles onto basic MCM-41-type solid supports. The supports were obtained by ion-exchange with Cs⁺ or K⁺ ions from both in-synthesis and post-synthesis Al-doped mesoporous molecular sieves MCM-41 (i.e., (Al)MCM-41 and Al-grafted MCM-41). For a comparison, Pd@Cs⁺-exchanged zeolite Y and the non-basic Pd@MCM-41 catalyst were also prepared. All supported catalysts were tested in Heck reaction of butyl acrylate and bromobenzene to give *n*-butyl cinnamate. Catalysts Pd@Cs⁺-(Al)MCM-41 and Pd@Cs⁺-Al-grafted MCM-41 proved to be superior to the analogous catalysts reported in the literature in terms of turnover number and turnover frequency. Most active, however, were catalytic systems obtained from combination of the simple, non-basic Pd@MCM-41 with an external base, which gave the coupling product in 33% after 20 h at 160 °C in *N,N*-dimethylacetamide in the presence of sodium acetate and at 1 mol.% palladium loading.

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1. Introduction

Palladium-catalyzed coupling reaction between activated alkenes and aryl or vinyl halides, so-called Heck reaction, is established as an efficient tool for the construction of new carbon–carbon bonds in polar molecules [1]. Continuing interest in the Heck reaction resulted in a remarkable extension in the scope of accessible substrates by means of tuning the properties of the catalytic system (palladium source, supporting ligands and base) and reaction conditions. Undoubtedly, the development of heterogeneous catalytic systems that do not require supporting ligands, typically phosphines, represents one of the most important recent achievements in this field [2].

In 1996, it has been shown for the first time that chemically generated palladium colloids can effect Heck reaction of styrene with aryl halides when combined with a proper base [3]. However, fine metal dispersions typically suffer from relatively low

stability and, hence, short life times. A substantial increase in the stability of metal dispersions has been achieved by using various supporting scaffolds such as polar additives and donating (co)solvents [4], polymers [5] and ionic liquids [6]. An alternative approach to stabilizing fine metal particles is represented by generation of reactive metal sites directly in an appropriate support [7]. The latter approach is particularly attractive for cross-coupling reactions as it principally allows for a simultaneous incorporation of both the metal catalyst and the necessary base into the solid support. This has been demonstrated by Corma and co-workers, who used ion-exchanged zeolites and sepiolite impregnated with palladium(II) chloride to prepare bifunctional catalysts. Unfortunately, bifunctional catalysts prepared in this manner exhibited relatively low activity in Heck reaction, requiring high catalyst loading (low substrate/Pd ratio) for the reaction to proceed satisfactorily [7d,e].

In this contribution, we report the preparation of supported bifunctional catalysts that combine palladium nanoparticles as the catalytically active sites and basic mesoporous molecular sieves (derived from MCM-41 by doping with Al-ions and cesium or potassium cations) as the halide scavenging sites.

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We present the details about the preparation and characterization of these novel catalysts and their non-basic counterpart and about their catalytic performance in Heck reaction between bromobenzene and butyl acrylate.

2. Results and discussion

2.1. Preparation and characterization of the catalysts

A series of supported catalysts consisting of simple (i.e., non-basic) and bifunctional ones has been prepared by deposition of palladium nanoparticles onto the selected molecular sieves. As the metal component, we have used chemically reduced palladium nanoparticles (see below) that proved to be the most active in our previous study on palladium-mediated condensation reaction between 2-aminoethanol and *cis*-1,4-butandiol [8]. On the other hand, we have tested several solid materials in order to assess the influence of the solid support on the reaction course. Thus, as a support for the non-basic catalyst we have chosen all-siliceous mesoporous molecular sieve MCM-41 (support I) while the basic bifunctional materials have been obtained from two MCM-41 sieves doped with Al(III) ions in both in-synthesis and post-synthesis manner. In the first case, an aluminum source (aqueous sodium aluminate) has been added directly to the sodium metasilicate/surfactant synthesis mixture to provide an MCM-41 type material with Al-sites distributed over the whole material ((Al)MCM-41, support II). In the second case, the accessible surface of all-siliceous MCM-41 has been modified with a thin layer of alumina by means of treatment with an aluminum chlorohydrate solution and subsequent calcination (Al-grafted MCM-41, support III) [9]. For a comparison, we have also employed commercial zeolite Y (support IV; Slovnaft VÚRUP, Slovakia, Si/Al=2.7).

Supports I–IV were ion-exchanged for cesium or potassium cations by stirring four times with 0.5 M aqueous cesium and potassium nitrate, respectively, washed thoroughly with deionized water and dried at 90 °C. Finally, the palladium nanoparticles were prepared in situ by chemical reduction of palladium(II) acetate with tetrabutylammonium acetate in tetrahydrofuran [4d]. Since the nanoparticles were deposited spontaneously onto the added mesoporous or zeolitic supports, the resulting supported catalysts were isolated by simple filtration and washing with diethyl ether. In view of our previous work [8] showing that complete removal of solvent leads to a decrease in the catalytic activity, the supported catalysts were not allowed to completely lose the stabilizing donor solvent (see Section 4 for details). In this manner, we have prepared a series of bifunctional basic catalysts: **1** (Pd@Cs⁺-(Al)MCM-41 from support II), **2** (Pd@Cs⁺-Al-grafted MCM-41 from support III), **3** (Pd@Cs⁺-zeolite Y from support IV), **4** (Pd@K⁺-(Al)MCM-41 from support II), **5** (Pd@K⁺-Al-grafted-MCM-41 from support III) as well as their non-basic counterpart **6** (Pd@MCM-41 from support I).

The catalysts were characterized by elemental analysis, IR spectra, X-ray powder diffraction and nitrogen adsorption isotherms. The content of palladium and alkali metal cations was determined by optical emission spectroscopy (ICP OES) on

Table 1
Analytical data for the catalysts

Catalyst	M	mmol M g ⁻¹	mmol Pd g ⁻¹
Catalyst 1	Cs	0.049	0.086
Catalyst 2	Cs	0.041	0.079
Catalyst 3	Cs	0.237	0.083
Catalyst 4	K	0.751	0.082
Catalyst 5	K	0.761	0.087
Catalyst 6	n.a.	n.a.	0.075

dried and mineralized samples while the chemical composition of the supports has been established by X-ray fluorescence analysis (Tables 1 and 2). All catalysts showed the palladium loading around 0.08 mmol g⁻¹. Since this value roughly corresponds to the reaction stoichiometry (0.1 mmol palladium(II) acetate per gram of dried support), we assume nearly complete reduction of the palladium precursor and deposition of the formed palladium particles.

The composition of the support and, hence, the acid–base properties of the catalysts were more diverse. In keeping with its chemical nature, the zeolite Y-based catalyst (catalyst **3**) accommodated the highest amount of Cs⁺ ions. Among the MCM-41-based materials, the K⁺-exchanged materials (catalysts **4** and **5**) exerted markedly higher alkali metal content than their Cs⁺-exchanged analogues (catalysts **1** and **2**), which is in accordance with the relative size of the alkali metal cations. On the other hand, the amount of the alkali metal ions did not differ much for the in-synthesis and post-synthesis modified materials (supports II and III → catalysts **1/4** and **2/5**).

In order to determine the *effective* amount of framework aluminum atoms, which corresponds to the total concentration of accessible basic centres, we followed adsorption of pyridine onto supports II and III by IR spectroscopy [10]. The spectra recorded before and after adsorption of pyridine (Fig. 1) showed clearly distinguishable peaks attributable to Brønsted (1545 cm⁻¹) and Lewis acid sites (1455 cm⁻¹). The determined amounts of acidic centres for supports II and III (Table 2) indicated Lewis acid sites

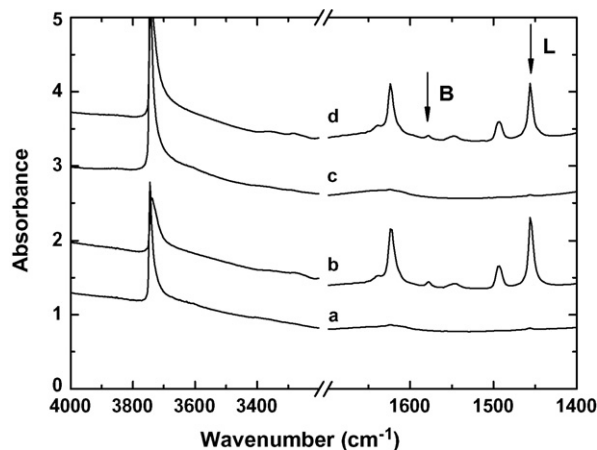


Fig. 1. FTIR spectra of free and pyridine treated supports II and III: support II (Al)MCM-41 before (a) and after (b) adsorption; support III (Al-grafted MCM-41) before (c) and after (d) adsorption. B and L denote peaks due to Brønsted and Lewis acid sites, respectively. For clarity, the spectra are vertically shifted.

Table 2

Acidic properties of aluminum containing mesoporous sieves as determined by FTIR and comparison with the analytical results from EDAX

Support	Acidic centres (mmol g ⁻¹)		Si/Al ratio ^a		Al sites (mmol g ⁻¹)
	Lewis	Brønsted	FTIR	XFS ^b	
Support II	0.25	0.04	29.5	19.8	0.55
Support III	0.38	0.05	20	6.9	0.81

^a Si/Al ratio for support IV as determined by chemical analysis was 2.2.

^b X-ray fluorescence spectroscopy.

to significantly prevail over the Brønsted ones in both cases. Support II exerted a notably higher Si/Al ratio, indicating a lower number of acid sites and, hence, a lower base loading after ion-exchange with alkali metal cations. In addition, a comparison of the aluminum content determined by elemental analysis data and the number of acid sites determined from pyridine adsorption revealed that the amount of accessible aluminum (acidic) sites is significantly lower than the total amount of aluminum atoms. The difference is particularly large for Al-grafted MCM-41 (support III) where the high aluminum content likely reflects a relatively high number of extra-framework, octahedrally coordinated aluminum atoms (Table 2).

X-ray powder diffractions patterns recorded for the mesoporous supports and catalysts prepared thereof were very similar, showing four distinguishable peaks in the region $2\theta < 10^\circ$. The catalysts exerted slightly lower diffraction intensities compared with their parent materials, which can be accounted for regularity lowering upon grafting of the palladium nanoparticles. Nonetheless, the similarity of the diffraction patterns for the supports and the catalysts corroborates that the hexagonal structure of the MCM-41 family remained unaffected by the treatment with the nanoparticles. In addition, the X-ray powder patterns were used to control the size of palladium nanoparticles by following the region of palladium (1 1 1) diffraction (see below) [11].

Nitrogen adsorption isotherms obtained with parent and modified MCM-41 samples were similar for the whole series, which

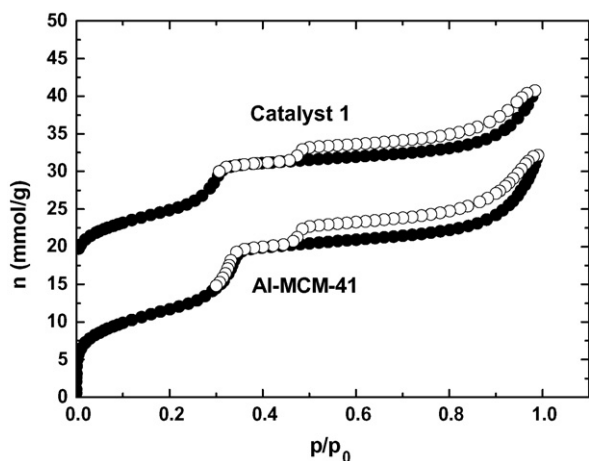


Fig. 2. Nitrogen adsorption isotherms for catalyst 1 and its parent (Al)MCM-41 (i.e., support II). For clarity, the isotherm for catalyst 1 is shifted by +15 mmol g⁻¹.

Table 3

Textural properties of the parent mesoporous molecular sieves and supported catalysts

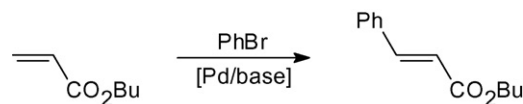
	S_{BET} (m ² g ⁻¹)	V_{meso} (cm ³ g ⁻¹)	d (nm)
Support I	913	0.622	4.0
Support II	955	1.04	4.0
Support III	778	0.620	4.0
Catalyst 1	818	0.453	4.0
Catalyst 2	546	0.403	3.9
Catalyst 3	301	–	–
Catalyst 6	897	0.660	4.0

is in accordance with X-ray diffraction data (see representative isotherms in Fig. 2). The isotherms displayed a sharp increase in the adsorbed amount at p/p_0 around 0.3–0.4, characteristic for hexagonal mesoporous molecular sieves possessing cylindrical pores with narrow pore size distribution. The calculated textural parameters (Table 3) indicated that grafting of the palladium nanoparticles has no significant effect on the pore size, slightly reducing surface areas and mesopore volumes. This corresponds to relatively low amount of palladium particles deposited.

2.2. Catalytic experiments

Catalytic activity of the prepared catalysts has been studied in Heck reaction of bromobenzene with butyl acrylate to give butyl cinnamate (Scheme 1). Typical kinetic profiles are shown in Fig. 3. The main parameters under study were catalyst support, external base and reaction solvent.

The results summarized in Table 4 show that all bifunctional catalysts are active in promoting the Heck coupling. The



Scheme 1.

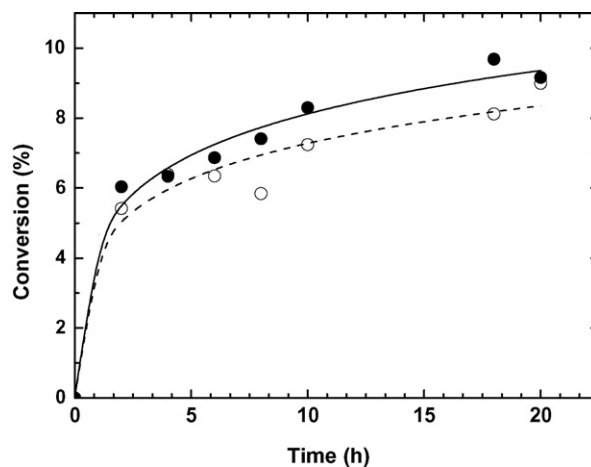


Fig. 3. Kinetic profiles of reaction catalyzed with catalysts 1 (○) and 2 (●). The lines were added to highlight the trends and do not represent a fit according to a kinetic model.

Cs⁺-exchanged catalysts exhibited higher conversions than their K⁺-exchanged congeners. The higher activity of Cs⁺-containing catalyst **2** as compared with **1** can be accounted for by a higher content of basic centres corresponding to the lower Si/Al ratio. Nonetheless, the Si/Al ratio is not the only factor being decisive for the catalyst activity as the most basic, zeolite Y-based catalyst **3** showed roughly similar conversions. The difference between zeolite Y and MCM-41 based materials stems likely from the substantial difference in the accessible surface area rather than from differences in chemical nature of the supports. While surface areas of mesoporous molecular sieves are larger than 800 m² g⁻¹ (catalysts **1** and **6**, cf. Table 3), that of zeolite Y is only 300 m² g⁻¹. Moreover, the polarity and size of the product molecules may prevent their desorption from channels of this zeolite.

In order to avoid a lack of usable base in the supported catalyst, we also tested palladium nanoparticles grafted onto a non-basic support, investigating the influence of an external base and the solvent (Table 4). The reaction in the presence of catalyst **6** without added base did not proceed at all. A survey of various reaction solvents and external bases performed with the non-basic catalyst **6** has shown *N,N*-dimethylacetamide to be the best solvent and anhydrous sodium acetate the most efficient base. When coupled, this optimized solvent-base combination ensued in conversion as high as 33% after 20 h at 160 °C (entry 14).

Leaching of the active phase during the catalyzed reactions is of critical importance for recycling of heterogeneous catalysts.

Table 4
Summary of catalytic results^a

Entry	Catalyst	Base	Solvent ^b	Conversion (%) ^c
1	1	–	DMA	8
2	1 (calcined)	–	DMA	6
3	1 (second run)	–	DMA	1
4	2	–	DMA	9
5	2 (calcined)	–	DMA	6
6	3	–	DMA	6
7	4	–	DMA	2
8	5	–	DMA	5
9	6	None	DMA	0
10	6	NBu ₃	DMA	17
11	6	NEt ₃	DMA	7
12	6	NEt(<i>i</i> -Pr) ₂	DMA	10
13	6	K ₂ CO ₃	DMA	21
14	6	NaOAc	DMA	33
15	6	Cs ₂ CO ₃	DMA	6
16	6	K ₃ PO ₄	DMA	13
17	6	NaOAc	TGDE	0
18	6	NaOAc	PC	4
19	6	NaOAc	DMF	15

^a The reactions were performed under nitrogen at 160 °C (150 °C for DMF) for 20 h with *n*-butyl acrylate (1.0 mmol), bromobenzene (1.5 mmol), a base (1.5 mmol, if appropriate) and 1,2-bis(2-methoxyethoxy)ethane (internal standard, 0.57 mmol) in 5 mL of solvent using catalyst amount corresponding to 1 mol% Pd with respect to *n*-butyl acrylate. See Experimental for details.

^b DMA, *N,N*-Dimethylacetamide; TGDE, 1,2-bis(2-methoxyethoxy)ethane or triethylene glycol dimethyl ether; PC, propylene carbonate; DMF, *N,N*-dimethylformamide.

^c Determined by gas chromatography.

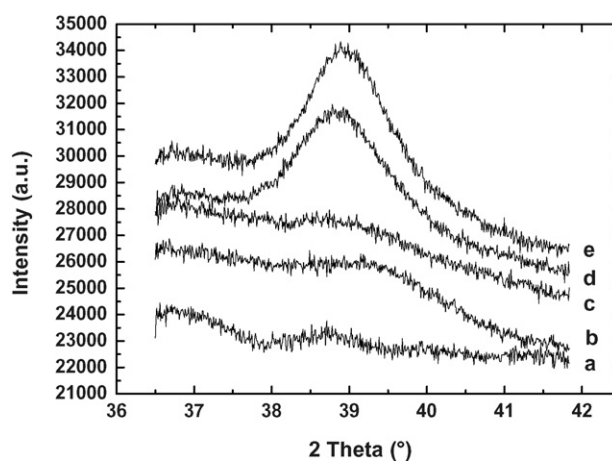


Fig. 4. X-ray powder diffraction patterns of catalyst **6** (a), catalyst **2** (b), catalyst **1** (c), and catalyst **1** recovered after one (d) and two (e) catalytic runs. The curves are shifted along the y-axis to avoid overlaps.

To determine the amount of palladium liberated from the support, the liquid part of the reaction mixture was filtered through a PTFE syringe filter (0.45 μm pore diameter) and analyzed for palladium by atomic emission spectroscopy. The amount of palladium in a liquid phase was found to be below the detection limit (0.6 ppb), which corresponds to a maximum concentration of 0.06 μg Pd/mL of the reaction liquid (i.e., below 0.3% of the palladium added to the reaction mixture). This provides clear evidence that no massive leaching of the metallic particles proceeded from the support. However, it is obvious from the collected conversion data that both repeated use and calcination of the bifunctional catalysts (see Table 4) resulted in a lowering of the catalytic activity. A lowering of the reaction rate even during the course of the single reaction is evident from the kinetic profiles (Fig. 3). The profiles have a burst-like shape, showing a steep increase in conversion within the first ca. 2 h after which the rate markedly drops. This can be accounted for by a growth of the metallic particles. A support for this explanation has been provided by a detailed X-ray diffraction study in the region of palladium (1 1 1) diffraction at $2\theta \approx 40^\circ$. The results presented

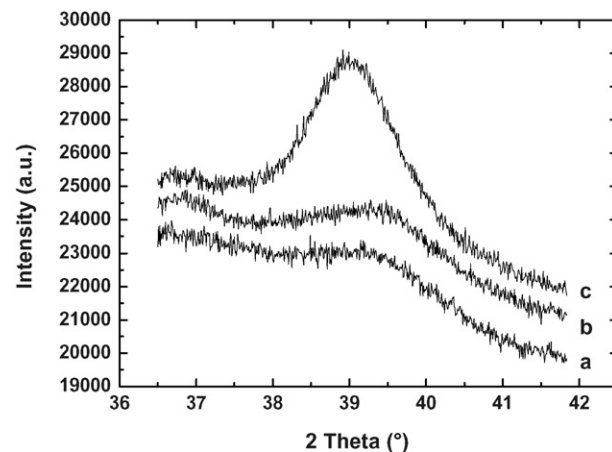


Fig. 5. X-ray powder diffraction pattern of fresh catalyst **2** new (a), catalyst **2** heated at 90 °C for after 2 h (b) and catalyst **2** recovered after one catalytic run (c). The curves are shifted along the y-axis to avoid overlaps.

in Fig. 4 clearly show an increase in the diffraction intensity for recycled catalysts attributable to a growth of the metallic particles and, hence, of the coherent diffraction volume [12]. Notably, calcination of the bifunctional supported catalyst prior to the use in Heck reaction (Fig. 5) had a similar effect. This clearly indicates that undesired particle growth occurs not only in the solution (via, e.g., desorption–aggregation–adsorption sequence or via uptake of chipped out metallic parts [13]) but also in the solid matrix. Since the reaction occurs only at relatively high temperatures (150–160 °C), the particle growth becomes an inevitable complication; the use of strongly stabilized particles may prevent their aggregation but will certainly make the metal species less reactive.

3. Conclusions

In summary, we have reported the preparation of bifunctional catalysts for Heck C–C bond coupling between bromobenzene and butyl acrylate based on combination of basic ion-exchanged Al-containing MCM-41 mesoporous molecular sieves and chemically generated palladium nanoparticles. The newly designed systems based on MCM-41 type materials proved to be more active than their analogue derived from ion-exchanged zeolite Y. When compared with the previous reports, the conversions observed with catalysts **1** and **2** are significantly lower (8% and 9%, respectively, using 1 mol% of Pd after 20 h) than those achieved with previously reported systems (98% conversion after 48 h has been observed in coupling between bromobenzene and styrene in refluxing *o*-xylene—however, with 34 mol% of Pd [7c]). In terms of catalyst efficiency expressed by turnover number (TON) and turnover frequency (TOF) [14], the newly designed catalysts **1** and **2** are also much more effective showing, respectively, TON/TOF of 8.0/0.4 and 9.0/0.45 h⁻¹ (cf. TON 2.9, TOF 0.06 h⁻¹ for the mentioned reference system). Nonetheless, the bifunctional catalysts are still significantly less active than a combination of their non-basic counterpart (Pd@MCM-41) with an external base which, with a proper solvent-base combination, gave the coupling product in 33% yield at catalyst loading corresponding to 1 mol% of Pd, which corresponds to TON = 33 and TOF = 1.7 h⁻¹.

4. Experimental

4.1. Materials

Three MCM-41-type materials were synthesized and used in this work: (i) all-siliceous MCM-41 (support I), (ii) (Al)MCM-41 with aluminum atoms incorporated during the synthesis of the mesoporous structure ((Al)MCM-41; support II) and (iii) after synthesis aluminium-grafted all-siliceous MCM-41 (Al-grafted MCM-41; support III). MCM-41 was prepared using sodium silicate (Riedel de Haen), hexadecyltrimethylammonium bromide (Fluka) and ethyl acetate (Fluka). The synthesis was carried out at 90 °C for 48 h and the template was subsequently removed by calcination at 550 °C for 6 h (for details, see Ref. [15]).

(Al)MCM-41 was synthesized similarly starting with sodium silicate (Riedel de Haen), sodium aluminate (Riedel de

Haen), hexadecyltrimethylammonium bromide (Fluka) and ethyl acetate (Fluka). The surfactant (9.80 g), sodium aluminate (0.32 g) and sodium silicate (10.0 g) were dissolved in water (950 mL; Si:Al molar ratio = 21). Ethyl acetate (15 mL) was added to the solution and the resulting mixture was thoroughly mixed, allowed to age at room temperature for 5 h and then heated at 90 °C for 60 h. The formed solid was filtered off while hot, washed out with water and calcined at 550 °C for 6 h.

In the preparation of Al-grafted MCM-41, all-siliceous MCM-41 obtained as given above was treated with a solution of aluminum chlorohydrate (0.6 g of 26% Al aluminum chlorohydrate and 50 mL of water per 1 g of MCM-41) at 70 °C for 2 h. The obtained material was filtered off, washed with water and calcined at 550 °C for 4 h (for details, see ref. [9]).

Zeolite Y (Slovnaft VÚRUP, Slovakia), palladium acetate (Aldrich), tetrabutylammonium acetate (Fluka), 1,2-bis(2-methoxyethoxy)ethane (Fluka), bromobenzene (Aldrich), *n*-butyl acrylate (Aldrich), *n*-butyl cinnamate (Alfa Aesar) and dry *N,N*-dimethylacetamide (Fluka) were used without further purification. Sodium acetate was freshly melted before use in order to remove traces of water. All catalysts were handled in air.

4.2. Methods

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 K α radiation ($\lambda = 1.5412 \text{ \AA}$) 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). Nitrogen adsorption isotherms were recorded with a Micromeritics ASAP 2020 volumetric instrument at –196 °C. The samples were degassed at 250 °C until pressure of 10⁻³ Pa was attained (for at least 24 h) prior to the measurements. X-ray fluorescence analysis was carried out with a Philips PW 1404 instrument using Uniquant Analytical software.

FTIR spectra were recorded on a Nicolet Magna-IR AEM spectrometer using a cell connected to a vacuum apparatus (64 scans, 4 cm⁻¹ resolution). Samples were pressed into self-supporting wafers with density of ca. 10 mg cm⁻². Samples used for the determination of acidic sites were first ion-exchanged with NH₄NO₃ (four times with excess 0.5 M aqueous solution), activated by evacuation and heating at 450 °C overnight and then treated with pyridine vapours at 150 °C for 20 min. An excess of pyridine was subsequently removed by a careful evacuation at the same temperature for 15 min. The following extinction coefficients were used to determine concentration of Lewis (ϵ_L) and Brønsted acid (ϵ_B) sites: $\epsilon_L = 2.22 \text{ cm} \mu\text{mol}^{-1}$ and $\epsilon_B = 1.67 \text{ cm} \mu\text{mol}^{-1}$ [10a].

The content of palladium, cesium and potassium was determined on an inductively coupled plasma optical emissions (ICP-OES) spectrometer (IRIS Intrepid II; Thermo Electron Corp.) equipped with axial plasma and ultrasonic CETAC nebulizer, model U-5000AT+ (conditions: plasma power 1150 W, nebulizer 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 dissolved in a mixture of concentrated HF and HNO₃ (volume ratio 2/3; Suprapur, Merck) at 50 °C for 15 min and diluted with re-distilled water.

The calibration curves were constructed using four points (blank and multi-element standards in 1% suprapure HNO₃) to cover the full range of the concentrations measured. The standards were prepared by diluting certified standard solution (Analytika). Analytical lines 324.270 nm for Pd and 766.491 nm for K were used. Due to technical restrictions of the detector, Cs content was quantified on a less sensitive line at 184.254 nm. Quality control was ensured by inserting QC sample into analytical run after measurement of an unknown sample.

4.3. Preparation of catalysts

4.3.1. Ion-exchange of aluminum containing MCM-41

(Al)MCM-41, Al-grafted MCM-41 and zeolite Y were ion-exchanged by stirring four times with 0.5 M solution of KNO₃ or CsNO₃ for 4 h at room temperature. Then, the mixture was filtered, the solid thoroughly washed with deionized water and dried at 90 °C.

4.3.2. Grafting of palladium nanoparticles

The mesoporous molecular sieve (1.00 g) was added to solution of palladium acetate (22.5 mg; 0.1 mmol), tetrabutylammonium acetate (94.5 mg; 0.315 mmol) in dry tetrahydrofuran and the mixture was refluxed for 4 h under argon atmosphere (for details, see refs. [4d,8]).

4.4. Catalytic tests

Catalytic tests were performed in Heidolph Synthesis I (system of 16-parallel reactions). The reaction mixture consisting of *n*-butyl acrylate (128 mg, 1.0 mmol), bromobenzene (236 mg, 1.5 mmol), a base (1.5 mmol) if appropriate, 1,2-bis(2-methoxyethoxy)ethane as an internal standard (100 mg, 0.57 mmol), solvent (5 mL) and catalyst in an amount corresponding to 0.01 mmol of palladium (1 mol% with respect to *n*-butyl acrylate), was heated at the reaction temperature (150 °C for DMF, 160 °C for all other solvents) under a nitrogen atmosphere for 20 h.

The composition of the reaction mixture was monitored by withdrawing aliquots that were first centrifuged at 4000 rpm for 10 min to remove the solids and subsequently analyzed by a high-resolution gas chromatography (Agilent 6850 chromatograph equipped with a flame ionization detector and DB-5 column, 10 m long, 0.1 mm in diameter and 0.1- μ m thick film). The identity of the reaction product was checked by GC-MS (Agilent 5975). For recycling experiments the catalysts were recovered from the reaction mixture by filtration, thoroughly washed with acetone and dried in air.

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