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The Heck arylation of mono- and disubstituted olefins catalyzed by palladium supported on alumina-based oxides

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ABSTRACT

Palladium catalysts containing Pd(0) or Pd(II) supported on alumina-based mixed oxides prepared by alkoxide sol-gel method (Al₂O₃, Al₂O₃-ZrO₂, Al₂O₃-ZrO₂-Eu₂O₃, Al₂O₃-MgO, Al₂O₃-CeO₂, Al₂O₃-Fe₂O₃) are very effective in the Heck coupling of bromobenzene with butyl acrylate in DMF solvent. In the presence of an excess of bromobenzene, butyl cinnamate (1) was formed as the main product after 4 h. With the same catalysts, good results, up to 97% yield of ethyl β -phenylcinnamate (3), were also obtained in the coupling of bromobenzene with ethyl cinnamate. The three most active catalysts, Pd(0)/Al₂O₃, Pd(II)/Al₂O₃, and Pd(II)/Al₂O₃-Fe₂O₃, were applied in the Heck cross-coupling of cinnamates with different bromobenzene and iodobenzene derivatives, leading to β -arylcinnamate products. The highest yield was observed when iodoanisole and cinnamic aldehyde were used as substrates. The formation of Pd(0) nanoparticles in the Heck reaction carried out with supported Pd(II) catalyst precursors was confirmed by TEM measurements.

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1. Introduction

The Heck cross-coupling reaction is recognized as one of the most important synthetic pathways to arylated olefins, important components for agrochemicals, pharmaceuticals, and cosmetics production.

Typical palladium catalysts used in the Heck reaction usually contain phosphorus ligands [1-11]; however, P-ligand-free systems containing Pd(OAc)₂, PdCl₂, or Pd(0) colloids have also been demonstrated recently to be highly active [5-21]. Phosphorus ligands are very often moisture and air sensitive, which creates problems in the catalytic system. In addition, there is a strong tendency to avoid application of these ligands because of their possibly negative impact on the natural environment.

Immobilized palladium species, preferably phosphorus-free, present a very attractive alternative to soluble palladium catalysts. Their main advantage is easier removal from the reaction mixture and possibility of recycling. In addition, the immobilized palladium catalysts containing very simple palladium precursors do not form any decomposition compounds that could contaminate the final organic product.

* Corresponding author. E-mail address: ania@wchuwr.pl (A.M. Trzeciak). A variety of supports have been used for P-ligand-less palladium catalysts designed for the Heck reaction, such as montmorillonite K-10 [22–24], alumina [25–28], MgLaO [29], zeolites [30–34], oxides of Ti, Zn, and Zr [35–39], MgO [38–40], Si/Al [41,42], hydrox-yapatite [43], layered double hydroxide (LDH) [44], chitosan [45], and modified silica [46–48]. Pd/C has also been studied intensively [49–52].

While in many cases high activity of these catalysts has been observed in the arylation of acrylates or styrene, very few studies have focused on their use in the synthesis of diarylated functionalized olefins such as β -arylcinnamates [53]. Typically, homogeneous systems containing phosphanes or tetraalkylammonium salts have been found more efficient for the preparation of diarylated functionalized olefins [54–59].

Thus, we decided to test palladium catalysts supported on different alumina-based oxides in order to find an efficient catalyst for the synthesis of diarylated functionalized olefins. Previously, we have studied palladium catalysts supported on Al₂O₃ in the Heck reaction of butyl acrylate with bromobenzene in [Bu₄N]Br medium [26]. Under such conditions, using an excess of bromobenzene, it was possible to obtain in one step the diarylated product, β -phenylcinnamate. It was also shown that the supported palladium catalysts act as a source of soluble Pd(II) complexes and Pd(0) nanoparticles, both catalytically active [26].

In this paper, we present studies of the catalytic activity of Pd(II) and Pd(0) immobilized on different alumina-based mixed oxides

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in the Heck reaction leading to mono- and diarylated olefin derivatives. The mixed metal oxides used as the supports for palladium nanoparticles might exhibit several advantages over usually used Al₂O₃. Alumina-zirconia oxides obtained by the sol-gel technique [60] are characterized by good thermal and mechanic stability [61-63]. Additionally, the Al₂O₃-ZrO₂ oxide containing 1% of Eu₂O₃ was also prepared [60] and tested as the catalyst support. It was expected that under the reaction conditions, Eu³⁺ could be reduced to Eu²⁺, possessing strong reducing properties and consequently facilitating stabilization of the catalytically active Pd(0) nanoparticles. Cerium dioxide is probably one of the most well investigated oxides among the rare-earth metal oxides and Al₂O₃-CeO₂ is a very suitable combination for preparing supports for immobilization of transitional metals. Ceria has various functions: it stabilizes alumina, keeps high surface area [64,65] and prevents the sintering of precious metals thus stabilizing their dispersed state [66]. The introduction of MgO to Al₂O₃ has effect on increasing hardness of the sol-gel-gel derived materials [67,68]. Similarly, the addition of Fe₂O₃ influences the structure of alumina improving its mechanical strength [69].

Using these alumina-based oxides as the supports for palladium, we expected to estimate the influence of the second metal oxide on the catalytic activity. The application of different supports for palladium catalysts could also allow us to formulate more general conclusions about the catalytic activity of heterogeneous systems in the synthesis of diarylated functionalized olefins.

2. Experimental

2.1. Preparation of alumina-based supports

The nanostructured Al₂O₃-ZrO₂ support containing 10% of ZrO₂ was prepared from AlO(OH) and ZrO(NO₃) xH₂O [60]. In the first step hydrolysis of Al(OⁱPr)₃ at 90 °C with continuous stirring gave AlO(OH). The suspension of AlO(OH) was added to the solution of $ZrO(NO_3) xH_2O$ in water containing HNO_3 ([Zr]:[NO_3]=1:4) and the mixture was heated at 90 °C for 72 h. The resulted transparent sol was condensed to obtain gel which was extruded in a wire form (2 mm in diameter), dried and calcined at 500 °C for 4 h. The obtained Al_2O_3 –ZrO₂ system is a porous material of 0.3 cm³/g total pores volume, characterized by a narrow pore distribution and developed specific surface BET equal to 220 m²/g. XRD and TEM studies of Al₂O₃-ZrO₂ samples have shown the presence of γ -Al₂O₃ phase whereas ZrO₂ most probably exists in an amorphous or highly dispersed form. The Al₂O₃-ZrO₂-Eu₂O₃ support was obtained by impregnation of Al₂O₃-ZrO₂ with an aqueous solution of Eu(NO₃)₃ for 24 h, followed by drying and calcination at 500 °C for 4 h [60].

Nanostructured supports consisting of Al₂O₃ as the main component and Mg, Fe(III) or Ce(IV) oxides were prepared by the same procedure using one-step aqueous sol–gel technique. The aluminium precursor, AlO(OH), was produced through hydrolysis of 102 g of solid Al(OⁱPr)₃ for 15 min in 600 cm³ of distilled water heated at 90 °C with continuous stirring. Thus obtained AlO(OH) was then peptized by slow addition of 2.86 cm³ of 65% nitric acid. Next, an aqueous solution containing the calculated amount of the respective nitrate (Mg, Fe or Ce) was added. The mixture was heated under reflux at 90 °C for 72 h and the resulted sol was concentrated by evaporation to obtain gel which was extruded in a wire form (2 mm in diameter), dried and calcined at 500 °C for 4 h yielding Al₂O₃-2%CeO₂, Al₂O₃-10%Fe₂O₃ or Al₂O₃-10%MgO.

2.2. Preparation of supported Pd(II) catalysts

First, 0.8 g of the support was impregnated, with stirring, in 10 cm^3 of an aqueous acidic solution ($C_{HCI} = 0.09 \text{ mol/dm}^3$) of PdCl₂,

containing 25 mg of Pd. After 72 h, the solution was decanted, and the Pd(II)-containing catalyst was washed three times with water and dried.

Palladium content was estimated by the ICP method, after mineralization of a weighted sample with aqua regia. The obtained palladium loading was from 1.3 to 1.9 wt.% in the final catalysts.

2.3. Preparation of supported Pd(0) catalysts

First, 25 cm^3 of an aqueous solution containing 0.5 cm^3 of $N_2H_4 \cdot H_2O$ (80%) was heated to $60 \circ C$. When the temperature was stabilized, the support containing Pd(II) was introduced to the hydrazine solution. Pd(II) was reduced to Pd(0) nanoparticles in 1 min, however the heating was continued for next 10 min. Finally, the obtained catalyst was washed with water and then dried in vacuo.

Palladium content was estimated by the ICP method, after mineralization of a weighted sample with aqua regia. The obtained palladium loading was from 1.3 to 1.9 wt.% in the final catalysts.

2.4. XRD and TEM measurements

The particle size and morphology of the catalyst samples were characterized using a FEI Tecnai G² 20 X-TWIN electron microscope (TEM) operating at 200 kV and providing 0.25 nm resolution. Specimens for TEM studies were prepared by putting a droplet of a colloidal suspension on a copper microscope grid covered with a perforated carbon film followed by evaporating the solvent under IR lamp for 15 min. The mean particle diameter and size distributions were calculated by counting at least 100 particles from the enlarged micrographs. The size distribution plots were fitted by means of a log-normal curve approximation.

The as-prepared and heat treated samples were characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using DRON-3 diffractometer (Ni-filtered CuK_{α} radiation); a scan rate of 0.5 deg/min was used to record the patterns in the 2 θ range of 20–80°.

Textural properties of sample samples (surface area, pore size distribution and pore volume) were determined by nitrogen adsorption-desorption isotherms at liquid nitrogen temperature by using an automatic volumetric apparatus (FISONS Sorptomatic 1900). Prior to measurements the samples were degassed for some hours at 300 °C and 10⁻³ Torr. The adsorption of nitrogen was followed until near saturation $(P/P_0 = 0.95)$, then the desorption was followed until the closure of the hysteresis loop. The adsorption data were interpreted by the application of a conventional BET method for determination of the surface area S_{BET} (m²/g). The total pore volume V_p (cm³/g) adsorbed near saturation was read from the adsorption isotherm. The pore size distribution was analyzed following the Dollimore-Heal method, which was applied to the desorption branch of each of the isotherms. The mean pore size R (nm) for each sample was read from the corresponding pore size distribution curve.

2.5. Heck reaction procedure

The Heck reaction of bromobenzene and butyl acrylate was carried out in a 50 cm^3 Schlenk tube with magnetic stirring. The reagents: catalyst containing 1.4×10^{-5} mol of palladium, PhBr 0.46 cm³ (4.36×10^{-3} mol), olefin (CH₂=CHC(O)OBu) 1.89×10^{-3} mol, NaHCO₃ (or other base, 4.76×10^{-3} mol) and DMF (5 cm^3), were introduced to the Schlenk tube under an Ar atmosphere. The reaction was carried out at 140 °C for 4 h. Afterwards, diethyl ether (10 cm^3) was added, and the sample was quenched with 10 cm^3 of water. The mixture was extracted with 2 portions of diethyl ether (10 cm^3 each), and an ether solution was analyzed

by GC (Hewlett Packard 8452A) with mesitylene as the internal standard.

The Heck reaction of an aryl halide $(2.0 \times 10^{-3} \text{ mol})$ with ethyl cinnamate (or cinnamic aldehyde, 1.89×10^{-3} mol) was carried out in a similar way. The organic products were identified by ¹H NMR and MS (GC-MS, Hewlett Packard 8452A) data. The product yields and substrate (olefin) conversion were determined by GC analysis.

For recycling experiments, only a solid catalyst was used. It was filtered off after the first reaction, washed with diethyl ether, dried and transferred to the Schlenk tube containing the organic substrates, base, and solvent.

Organic products **1–12** were identified by ¹H NMR (Bruker 300 and 500 MHz) and MS data. Products **1**, **2** [26] and **5**, **7**, **8** and **9** [70] were characterized by comparison with their reported data.

2.6. (3) Ethyl β -phenylcinnamate

MS: m/z (%) 252(M⁺, 86), 223(24), 207(100), 178(90), 152(21), 105(24), 77(21), 51(17) up to 3% of (E+Z) ethyl α -phenylcinnamates was also found:

MS: *m/z* (%) 252(M⁺, 76), 207(14), 179(100), 152(14), 135(66), 107(48), 77(14), 51(10).

MS: m/z 252(M⁺, 72), 207(24), 179(100), 152(14), 135(62), 107(45), 77(14), 51(10).

2.7. (4)-Ethyl β -(4-formylphenyl)cinnamate

E: ¹H NMR (CDCl₃) δ , ppm: 1.18 (*t*, *J*=7.1 Hz, 3H, CH₃), 4.01 (*q*, *J*=7.1 Hz, 2H, CH₂), 6.5 (s, 1H, vinyl), 7.27–7.28 (m, 2H, aryl), 7.45–7.46 (m, 3H aryl), 7.5 (d, *J*=8.3 Hz, 2H, aryl) 7.8(d, *J*=8.3 Hz, 2H, aryl), 10.07 (s, 1H, CHO).

MS: *m/z* (%) 280(M⁺, 96), 251(27), 235(94), 208(54), 178(100), 152(17), 105(23), 77(21), 51(17).

Z: ¹H NMR (CDCl₃) δ , ppm: 1.28(t, J=7.1 Hz, 3H, CH₃), 4.4(q, J=7.1 Hz, 2H, CH₂), 6.51(s, 1H, vinyl), 7.27–7.28 (m, 2H, aryl), 7.45–7.46 (m, 3H aryl), 7.5 (d, J=8.3 Hz, 2H, aryl) 7.8(d, J=8.3 Hz, 2H, aryl), 10.12(s, 1H, CHO).

MS: m/z (%) 280(M⁺, 79), 251(21), 235(77), 208(48), 178(100), 152(17), 105(23), 77(19), 51(15) up to 3% of (E+Z) ethyl α -(4-formylphenyl)cinnamates was also found:

MS: *m*/*z* (%) 280(M⁺, 100), 235(11), 207(63), 178(89), 152(11), 135(74), 107(37), 77(11), 51(8).

MS: *m/z* (%) 280(M⁺, 100), 235(16), 207(58), 178(74), 152(11), 135(58), 107(32), 77(11), 51(8).

2.8. (10)- β -(4-Methyl)cinnamic aldehyde

E: MS: m/z (%) 222(40), 221(52), 208(17), 207(100), 189(8), 179(27), 178(41), 165(9), 152(7), 115(24), 102(19), 89(10), 77(6). Z: MS: m/z (%) 222(42), 221(52), 208(16), 207(100), 189(7), 179(27), 178(41), 165(9), 152(7), 115(24), 102(19), 89(10), 77(6).

2.9. (11)- β -Phenylcinnamic aldehyde

MS: *m*/*z* (%) 208(76), 207(100), 179(31), 178(47), 152(10), 131(10), 105(7), 102(36), 77(12), 51(24).

2.10. (12) β -(4-Methoxyphenyl)cinnamic aldehyde

E: MS: *m*/*z*(%) 238(M⁺, 100), 223(16), 207(38), 178(15), 165(48), 135(19), 132(20), 102(38), 89(17), 63(13), 39(8).

Z: MS: m/z (%) 238(M⁺, 100), 223(15, 207(42), 178(17), 165(52), 135(19), 132(20), 102(40), 89(17), 63(13), 39(8) up to 10% of 4,4'-dimethoxybiphenyl was also formed as a result of homo-coupling of iodoanisole

MS: m/z (%) m/z 214(100), 199(84), 171(26), 156(11), 139(5), 128(16), 107(5)

3. Results and discussion

3.1. Characterization of alumina-based oxides

XRD diffraction patterns of alumina and a set of the aluminabased mixed oxides have been recorded. The peaks in the diffractogram of alumina (Fig. 1a) at 37.6°, 45.8° and 66.6° are very close to those reported for crystalline γ -Al₂O₃ (JCPDS no. 10-0425) and might be attributed to the (331), (400) and (440) planes. respectively. These signals are also observed in the diffractograms of the Al₂O₃-10%Fe₂O₃ (Fig. 1d) and Al₂O₃-2%CeO₂ (Fig. 1b) samples. Moreover, two very weak diffraction peaks at around 33.3° and 35.8° in the first case, and a broad peak at 28.6° in the second case may be observed indicating the formation of α -Fe₂O₃ and CeO₂ phases according to JCPDS file no. 13-0534 and 34-0394, respectively. The large width of these peaks might be accounted for the presence of very small particles. These results also reveal that probably no solid solutions are formed and these mixed oxides are composed of highly dispersed α -Fe₂O₃ and CeO₂ particles. The XRD results obtained for the Al₂O₃-10%MgO sample (Fig. 1c) suggest the formation of alumina solid solution: the characteristic signals of γ -Al₂O₃ are shifted towards lower 2 θ positions; for instance, Al₂O₃ (440) reflection at 66.6° is moved to 66.1°. No MgO phase is detected indicating that all amount of MgO (10%) was incorporated into the structure of alumina to form a typical solid solution. According to literature [71,72], MgO content up to 30% may form solid solutions with alumina without presence of MgO phase. Generally, broad reflections that are observed for both alumina and the alumina-based solid solutions indicate fine particle nature of the obtained materials. The average Al₂O₃ crystallite size is about 4 nm, as determined from the X-ray line broadening using Scherrer's formula.

Taking into account the adsorption–desorption isotherms with corresponding pore size distributions (shown in Fig. 2) and the calculated values of both the specific surface area (S_{BET}) and mean pore diameter (R), listed in Table 1, it could be noted that all the prepared samples are mesoporous in nature. The nitrogen adsorption–desorption isotherms are of Type IV and exhibit the characteristic H2 hysteresis loop for mesoporous materials according to IUPAC classification. However, the textural properties of the prepared samples are different, influenced by the



Fig. 1. XRD diffractograms of alumina (a) and mixed oxides: $Al_2O_3-2%CeO_2$ (b), $Al_2O_3-10\%MgO$ (c), $Al_2O_3-10\%Fe_2O_3$ (d) and comparison with ASTM data.



Fig. 2. N_2 adsorption-desorption isotherms and corresponding pore size distributions of alumina (a) and mixed oxides: $Al_2O_3-2\%CeO_2$ (b); $Al_2O_3-10\%MgO$ (c) and $Al_2O_3-10\%Fe_2O_3$ (d).

 Table 1

 Textural properties of the supports in comparison to the pure alumina.

Sample	$S_{\rm BET}~(m^2/{ m g})^{ m a}$	R (nm) ^b	$V_p (cm^3/g)^c$
Al ₂ O ₃	210	4.8	0.31
Al ₂ O ₃ -10%ZrO ₂ [60]	218	2.2	0.27
Al ₂ O ₃ -10%ZrO ₂ -1%Eu ₂ O ₃ [60]	182	2.7	0.25
Al ₂ O ₃ -2%CeO ₂	170	9.5	0.51
Al ₂ O ₃ -10%Fe ₂ O ₃	210	3.8	0.21
Al ₂ O ₃ -10%MgO	158	7.8	0.23

^a Specific surface area (according BET method).

^b BJH method desorption pore diameter.

^c Total pore specific volume (at $P/P_0 = 0.99$).

addition of another metal oxide to γ -alumina. It is expected that the textural properties of the mixed oxides result both from the number of hydroxyl groups on the surface and the interactions between all the components added during the preparation process. Pore size distributions (inset of Fig. 2) are monomodal for all the samples. The Al₂O₃-10%Fe₂O₃ mixed oxide is characterized by a slightly shifted (compared to pure alumna) sharp curve centered at 3.8 nm, while considerably broad pore size distributions are observed for the other oxides (Al₂O₃-10%MgO and Al₂O₃-2%CeO₂). It should be noted that the mean pore size diameter is moved to higher values and centered at 7.8 or 9.5 nm for the Al₂O₃-10%MgO and Al₂O₃-2%CeO₂ samples, respectively. The addition of a metal nitrate to aluminium hydroxide during sol-gel preparation leads to a decrease of the BET specific surface area of the resulting alumina-based mixed oxides: 210, 170 and $158 \text{ m}^2/\text{g}$ for the Al₂O₃-10%Fe₂O₃, Al₂O₃-2%CeO₂ and $Al_2O_3 - 10\%MgO$ samples, respectively, in comparison to $218 \text{ m}^2/\text{g}$ for the pure γ -alumina. The drop of S_{BET} on the order of 4–27% (especially in case of Al₂O₃-10%MgO or Al₂O₃-2%CeO₂) and shift to a larger pore diameter show that the introduced metal oxides considerably modify the textural properties of γ -alumina. Additionally, a variation in the total pore volume with the sample composition is also observed. The Al₂O₃-10%MgO and Al₂O₃-10%Fe₂O₃ oxides showed a lower volume ($\sim 0.2 \text{ cm}^3/\text{g}$) in comparison to the pure γ -alumina (~0.3 cm³/g), while the total pore volume observed for the Al₂O₃-2%CeO₂ mixed oxide increased to \sim 0.5 cm³/g. Therefore, cerium oxide, which does not form a bulk solid solution with Al₂O₃, significantly modifies the porosity of γ -alumina (Table 1).

3.2. Characterization of supported Pd(II) and Pd(0) catalysts

The morphology of the Pd(II)/Al₂O₃ catalyst precursor was characterized by Z-contrast imaging with high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). The obtained micrograph (Fig. 3) reveals that palladium is not uniformly dispersed on the surface of the support. It forms islands with an average diameter of about 10–15 nm. Very often these islands are observed directly on the surface of rather thin fragments of Al₂O₃, not necessarily in the pores of the support. High resolution TEM confirmed that the adsorbed Pd(II) species are amorphous, no crystalline structure could be observed. Most probably they form a very thin layer which is easily dissolved during the catalytic reaction.

Pd(0) catalysts supported on alumina-based oxides have been obtained from supported Pd(II) using hydrazine as the reducing agent. TEM investigations have been performed on three selected catalysts supported on Al_2O_3 , Al_2O_3 – Fe_2O_3 and Al_2O_3 – CeO_2 . The obtained micrographs evidenced the presence of Pd(0) in form of nanoparticles in all of the tested samples. The nanoparticles size is practically the same for Pd(0) catalysts supported on Al_2O_3 and Al_2O_3 – Fe_2O_3 . The observed particle diameter is in range 4–15 nm and the average size is 7–8 nm. Slightly bigger nanoparticles have been obtained on Al_2O_3 – CeO_2 support, the average Pd(0) diameter is about 12 nm.



Fig. 3. TEM bright field image (left) and corresponding HAADF STEM micrograph (right) of the Pd(II)/Al₂O₃ catalyst precursor.



Scheme 1.

3.3. Catalytic activity of Pd supported on alumina-based oxides in Heck reaction

The Heck reaction was carried out in DMF as a solvent, with an excess of bromobenzene versus butyl acrylate ([PhBr]:[$CH_2=CHCO_2Bu$]=2.3). Under such conditions, it was possible to obtain two products, butyl cinnamate **1** (only the trans-isomer is formed) and butyl phenylcinnamate **2**, in one stage (Scheme 1).

In the reaction carried out with $Pd(0)/Al_2O_3$ without any base, 71% of the monoarylated product **1** was obtained. The effect of different bases on the composition of the reaction products is shown in Table 2. In most cases, **1** was the main product; only in the presence of NaHCO₃ **2** was found with 29% yield. The best results were obtained with NaHCO₃ and NaOAc; therefore, these two bases were applied in further experiments.

Kinetic studies performed for the $Pd(0)/Al_2O_3$ catalyst in DMF in the presence of both bases, NaHCO₃ and NaOAc, showed that product **2** was formed only when the conversion of the substrates to product **1** had reached 100% (Fig. 4). Thus, it was possible to obtain product **1** with high selectivity breaking the reaction after an appropriate length of time.

To examine whether a similar feature is also characteristic for Pd(II) catalysts a competition experiment was performed, in which an equimolar mixture of ethyl cinnamate and butyl acrylate was used as the substrate. This reaction, catalyzed with Pd(II)/Al₂O₃-Fe₂O₃, started without any induction period however

Table 2

Catalytic activity of $Pd(0)/Al_2O_3$ in the Heck reaction in DMF with different bases (reaction products 1 and 2 see Scheme 1).

Base	Olefin conversion (%)/product yield 1:2 $Pd(0)/Al_2O_3$		
-	71 71:0		
NaHCO ₃	100 71:29		
NaHCO3 ^a	100 95:5		
HCOONa	65 65:0		
Bu ₃ N	52 52:0		
NaOAc	100 97:3		
Et ₃ N	62 62:0		
Cs ₂ CO ₃	83 83:0		

[Pd] (1.4×10^{-5} mol); PhBr (4.36 mmol); butyl acrylate (1.89 mmol); mesitylene as the internal standard (0.715 mmol); base (4.76 mmol); DMF (5 ml); $140 \circ$ C; 4 h; Ar. ^a $130 \circ$ C.



Fig. 4. The yield of products **1** and **2** formed in the Heck reaction catalyzed by Pd(0)/Al₂O₃. [Pd] (1.4×10^{-5} mol); PhBr (4.36 mmol); butyl acrylate (1.89 mmol); mesitylene as the internal standard (0.715 mmol); NaHCO₃ (4.76 mmol); DMF (5 ml); 140 °C; Ar.

only the acrylate was converted to product **1**. After 4 h 92% of butyl acrylate reacted, whereas ethyl cinnamate remained completely unreacted.

Figs. 5 and 6 illustrate the catalytic activity of the supported Pd(0) and Pd(II) catalysts. In all cases, the monoarylated product ${\bf 1}$



Fig. 5. Results of the Heck reaction with different Pd(0) supported catalysts (reaction products **1** and **2** see Scheme 1. [Pd] $(1.4 \times 10^{-5} \text{ mol})$; PhBr (4.36 mmol); butyl acrylate (1.89 mmol); mesitylene as the internal standard (0.715 mmol); NaHCO₃ (4.76 mmol); DMF (5 ml); 140 °C; 4 h; Ar.



Fig. 6. Results of the Heck reaction with different Pd(II) supported catalysts (reaction products **1** and **2** see Scheme 1. [Pd] $(1.4 \times 10^{-5} \text{ mol})$; PhBr (4.36 mmol); butyl acrylate (1.89 mmol); mesitylene as the internal standard (0.715 mmol); NaHCO₃ (4.76 mmol); DMF (5 ml); 140 °C; 4 h; Ar.

dominated; however, formation of **2** in amounts of up to 29% was observed in some reactions catalyzed by Pd(0). The effect of the kind of support on the Heck reaction yield appeared to be not very significant, and the presence of ca. 10% of Fe₂O₃ or MgO as well as 2% of CeO₂ had no significant impact on the reaction yield, which was over 80% in almost all cases. Regardless of the kind of the support, Pd(0) was in most cases more productive than Pd(II), especially in respect to the yield of **2**. It can be concluded that the reduction of palladium before the Heck reaction to the form of supported Pd(0) nanoparticles has a positive effect on the reaction course because both types of catalysts, containing Pd(II) or Pd(0), originated from the same precursor.

To check whether the supported catalysts are also active in the synthesis of diarylated functionalized olefins under the same conditions, the coupling of ethyl cinnamate with bromobenzene was selected as a test reaction (Scheme 2 and Fig. 7). Surprisingly, in this reaction, better results were obtained for immobilized Pd(II) used without earlier pre-treatment. The highest yield, 95% and 87%, was found for Pd(II)/Al₂O₃ and Pd(II)/Al₂O₃–Fe₂O₃. A relatively good result, 76% yield, was also obtained for Pd(0)/Al₂O₃.



Fig. 7. Results of the Heck reaction with different Pd(0) and Pd(II) supported catalysts according to Scheme 2. [Pd] $(1.4 \times 10^{-5} \text{ mol})$; PhBr (2.0 mmol); ethyl cinnamate (1.89 mmol); mesitylene as the internal standard (0.715 mmol); NaHCO₃ (4.76 mmol); DMF (5 ml); 140 °C; 4 h; Ar.

These three catalysts were selected for further studies oriented towards synthesis of β-arylcinnamates in reactions of iodo- or bromobenzene derivatives containing activating or deactivating substituents in the phenyl ring. In these experiments, ethyl cinnamate or cinnamic aldehvde was used as the olefinic substrate (Scheme 3). To obtain comparable results, all the experiments were performed over the same length of time, 4 h. The coupling products were obtained with moderate-to-excellent vield for all three of the catalysts studied. Differences between the catalysts were small; however, slightly higher yield of the products was observed for Pd(II)/Al₂O₃-Fe₂O₃ in reactions with NaHCO₃ as the base. When NaOAc was used instead, the yield of the product decreased, but at the same time the E:Z selectivity increased. Only in the reaction of 4-bromobenzaldehyde with ethyl cinnamate, did the application of NaOAc lead to an increase in both yield and the E:Z ratio. The highest yields of ethyl β -arylcinnamates were obtained in the reactions of ethyl cinnamate with bromobenzene and with iodoanisole (Table 3).

Consequently, excellent results (100% yield) were also obtained in the reaction of iodoanisole with cinnamic aldehyde. On the other



Scheme 3.

Table 3
Results of the Heck reaction according to Scheme 3 – formation of diarylated olefins with Pd(0) and Pd(II) supported catalysts

X	R	R^1	Product no.	Base	Yield (%) ^a (E:Z)		
					Pd(0)/Al ₂ O ₃	$Pd(II)/Al_2O_3$	Pd(II)/Al ₂ O ₃ -Fe ₂ O ₃
Br	Н	CO ₂ Et	3		76	95	87
Br	4-CHO	CO ₂ Et	4	NaHCO ₃	37 (72:28)	44 (71:29)	44 (71:29)
Br	4-CHO	CO ₂ Et	4	NaOAc		60 (83:17)	60 (81:19)
Br	4-C(O)Me	CO ₂ Et	5	NaHCO ₃	36 (63:37)	51 (63:37)	54 (62:38)
Br	2-Me	CO ₂ Et	6	NaHCO ₃	7	8	7
Br	4-Me	CO ₂ Et	7	NaHCO ₃	77 (60:40)	71 (60:40)	82 (60:40)
Br	4-Me	CO ₂ Et	7	NaOAc		53 (78:22)	30 (83:17)
Br	4-OMe	CO ₂ Et	8	NaHCO ₃		76 (57:43)	85 (57:43)
Br	4-OMe	CO ₂ Et	8	NaOAc		66 (73:27)	35 (78:22)
I	4-Me	CO ₂ Et	7	NaHCO ₃	72 (71:29)	65 (71:29)	68 (70:30)
Ι	4-OMe	CO ₂ Et	8	NaHCO ₃	82 (72:28)	84 (72:28)	90 (73:27)
Ι	4-OMe	CO ₂ Et	8	NaOAc		65 (75:25)	58 (75:25)
I	4-OMe	CHO	8	NaHCO ₃		100 (64:36)	100 (65:35)
Br	C_6H_4	CO ₂ Et	9	NaHCO ₃	8 (36:64)	20 (37:63)	22 (36:64)
I	C_6H_4	CO ₂ Et	9	NaHCO ₃	36 (55:45)	36 (57:43)	45 (55:45)
Br	4-Me	CHO	10	NaHCO ₃		53 (60:40)	67 (63:37)
Br	Н	CHO	11	NaHCO ₃		72	62
Br	4-OMe	CHO	12	NaHCO ₃		42 (63:37)	54 (75:25)

[Pd] (1.4 × 10⁻⁵ mol); ArX (2.0 mmol); ethyl cinnamate or cinnamic aldehyde (1.89 mmol); mesitylene as the internal standard (0.715 mmol); base (4.76 mmol); DMF (5 ml); 140 °C; 4 h; Ar.

^a Conversion to the coupling product determined by GC.

hand, bromobenzene derivatives substituted in position 2 do not form any coupling products under the conditions applied. Only for 2-bromotoluene a cross-coupling product was obtained with the yield up to 8%.

The E:Z values obtained with supported palladium catalysts are very similar to those reported for homogeneous catalytic systems containing $Pd(OAc)_2/PPh_3/[Bu_4N]Br$ [59]. When we used such a catalytic system for the coupling of 4-iodoanisole with ethyl cinnamate, 100% yield of the product was obtained after 4h with E:Z=70:30.

3.4. Recycling of Pd supported on alumina-based oxides in Heck reaction

For the reuse studies, the catalyst was separated from the reaction mixture by filtration immediately after the catalytic reaction, washed with diethyl ether, and dried. In such a procedure, the presence of any soluble palladium species leached from the catalyst was minimized. Two series of experiments were performed with $Pd(0)/Al_2O_3$: without any base and with NaHCO₃ using bromobenzene and butyl acrylate as the substrates (Table 4). In the first case, only product **1** was formed, and its amount decreased from 71% in the first reaction to 42% in the third one. The presence of a base contributed to a higher yield of the products with some decrease in the subsequent runs, from 100% in the first to 76% in the third one. The yield of product **2** also decreased at the same time.

In our earlier studies of the Heck reaction in molten $[^{n}Bu_{4}N]Br$ as the reaction medium, we compared the results for the recycling of a Pd/Al₂O₃ catalyst carried out in two different ways [26]. In the first procedure, the reaction products were extracted with diethyl ether after the first run, and for the second run, the catalyst was used together with [^{*n*}Bu₄N]Br, which contained soluble palladium compounds eluted from the support in the first run. Using this procedure, we obtained ca. 100% of butyl acrylate conversion even in the third run (Table 4) [26]. When the product separation procedure was changed and only the heterogeneous Pd/Al₂O₃ catalyst, separated from the reaction mixture and carefully washed with diethyl ether, was used for the second run, the observed conversion of butyl acrylate dropped to ca. 10% already in the third run [26]. Thus, these results indicated that soluble palladium species, like anionic Pd(II) complexes of [PdPhX₃]⁻ type or Pd(0) nanoparticles stabilized with ammonium salt [16,45,55], contributed remarkably to the catalytic activity of $Pd(0)/Al_2O_3$ when the reaction was performed in [^{*n*}Bu₄N]Br. It is worth to note, that the results of the Heck reaction are practically independent on the kind of Pd precursor used (Pd/Al₂O₃, PdCl₂(PhCN)₂, Pd/PVP) in [ⁿBu₄N]Br as reaction medium [16,17,26].

The procedure used in this paper is similar to that described above as the second one, however, the product yields obtained

Table 4

Recycling test of different palladium catalysts of Heck reaction (Scheme 1) performed in DMF and ["Bu₄N]Br as reaction medium.

Catalyst	Base/solvent	Olefin conversion (%)/product yield 1:2		
		Run 1	Run 2	Run 3
$Pd(0)/Al_2O_3$	–/DMF	71	67	42
		71:0	67: 0	42:0
$Pd(0)/Al_2O_3$	NaHCO ₃ /DMF	100	92	76
		77:23	88:4	76: 0
Pd(0)/Al ₂ O ₃ [26]	NaHCO ₃ /[Bu ₄ N]Br ^a	100	100	100
		17:83	22: 78	46: 54
Pd(II)/Al ₂ O ₃ [26]	NaHCO3/[Bu4N]Br ^b	100	100	10
		1:99	4:96	

[Pd] (1.4 × 10⁻⁵ mol); PhBr (4.36 mmol); butyl acrylate (1.89 mmol); mesitylene as internal standard (0.715 mmol); NaHCO₃ (4.76 mmol); DMF (5 ml) or [^{*n*}Bu₄N]Br (0.75 g); 140 °C; 4 h; Ar.

 $^a~Pd/Al_2O_3$ catalyst was used in the next run together with $[Bu_4N]Br$ phase [26].

^b Pd/Al₂O₃ catalyst was separated, washed, dried and used in the next run [26].

Table 5

Diameters of Pd(0) nanoparticles supported on various alumina-based oxides observed in TEM before and after the Heck reaction.

Sample	Nanoparticles size (nm) ^a	Typical diameter (nm) ^b	Size distribution ^c
Pd(0)/Al ₂ O ₃ before reaction	4-15	7	-
Pd(0)/Al ₂ O ₃ after reaction	4–15	7	<i>d</i> = 8.3 nm
			FWHM = 4.8 nm
Pd(II)/Al ₂ O ₃ after reaction	4–15	9	<i>d</i> = 9.8 nm
			FWHM = 6.3 nm
Pd(0)/Al ₂ O ₃ -Fe ₂ O ₃ before reaction	4–16	8	-
Pd(0)/Al ₂ O ₃ -Fe ₂ O ₃ after reaction	4–16	8	<i>d</i> = 8.8 nm
			FWHM = 4.3 nm
Pd(II)/Al ₂ O ₃ -Fe ₂ O ₃ after reaction	8-32	18	<i>d</i> = 19.9 nm
			FWHM = 10.1 nm
Pd(0)/Al ₂ O ₃ -CeO ₂ before reaction	5–20	12	-
Pd(0)/Al ₂ O ₃ -CeO ₂ after reaction	5–20	12	-
Pd(II)Al ₂ O ₃ -CeO ₂ after reaction	5–20	15	-

^a Total range of observed nanoparticle diameters.

^b Most characteristic nanoparticle size in a sample.

^c Log-normal fit of nanoparticle size distribution.

in DMF are much higher than those reported previously for tetrabutylammonium bromide [26]. Thus, participation of the leached palladium forms acting as homogeneous catalysts seems to be smaller in the Heck reaction carried out in DMF than in molten tetrabutylammonium salts. Palladium leaching in the studied systems was estimated on the basis of Pd content in the supported catalysts separated after the Heck reaction. ICP analyses performed immediately after hot filtration showed that up to 25% of palladium leached in case of the Pd(0) catalyst precursors and even 50% when Pd(II) precursors had been



Fig. 8. TEM micrographs showing structure of Pd(0)/Al₂O₃ after the Heck reaction (a) and Pd(0) nanoparticles formed in situ from Pd(II)/Al₂O₃ precursor under the Heck reaction conditions (b).



Fig. 9. TEM micrographs showing structure of Pd(0)/Al₂O₃-Fe₂O₃ after the Heck reaction (a) and Pd(0) nanoparticles formed in situ from Pd(II)/Al₂O₃-Fe₂O₃ precursor under the Heck reaction conditions (b).

used. Similarly, the XRD measurements also showed higher content of supported palladium in the $Pd(0)/Al_2O_3$ catalyst recovered after the Heck reaction.

It is well documented in the literature that the concentration of soluble palladium leached from the support decreases remarkably at the end of a catalytic reaction as a result of redeposition [14,28]. To check the level of Pd readsorption in our systems a sample of Pd(II)/Al₂O₃ was analyzed immediately after the Heck coupling of ethyl cinnamate with bromobenzene. After that process 47% of palladium was found on the support. The same sample of the catalyst was left in the post-reaction mixture at room temperature for next 2 days and after that time the palladium content was estimated again. The ICP analysis gave practically the same result, 46.6% of the initial amount of palladium. Thus, it might be concluded that Pd leaching is irreversible in those systems.

To estimate the role of soluble palladium species in the Heck coupling of ethyl cinnamate with bromobenzene a comparative experiment was performed under the same conditions with soluble Pd(OAc)₂ used as the catalyst. The yield of the product with 1.4×10^{-5} mol Pd was 32% after 4 h and it was remarkably lower than with the supported Pd(II) catalysts. Interestingly, when an analogous reaction catalyzed with Pd(OAc)₂ was carried out in the presence of pure Al₂O₃ support, the yield of **1** increased to 58% after 4 h indicating the positive effect palladium immobilization on the

catalytic efficiency. Similarly, it has been recently found that the immobilized Pd(II) is more active than soluble Pd(II) complexes in the Heck reaction of cyclohexene with bromobenzene [73].

To discuss further the role of the leached palladium in the catalytic process a hot filtration test was performed for the Heck reaction catalyzed with $Pd(II)/Al_2O_3$. The reaction mixture was filtered after 1 h of reaction, when the yield of product was 45%. Next, the solution was heated (140 °C) for 3 h without catalyst and during that time the yield increased to 54%. In the reference sample, not filtrated, 84% of **1** was found after 4 h. Thus, it might be assumed, in agreement with reports of other authors [18–20,46], that the leached palladium contains catalytically active molecular Pd species and catalytically inactive Pd clusters, both remaining in equilibrium in the reaction mixture. The real contribution of these forms in our systems is under studies.

3.5. TEM studies of Pd supported on alumina-based oxides

TEM method was used to characterize the supported palladium catalysts before and after the Heck reaction. The observed range of the nanoparticle size and average diameter (Table 5) is practically the same for the as-prepared supported Pd(0) catalyst precursors and the Pd(0) catalysts recovered after the Heck reaction carried out in DMF as the solvent (Scheme 1).

The Pd(0) nanoparticles supported on Al₂O₃ are spherical and none of them show typical crystal outlines (Fig. 8a). They have similar diameters (the maximum of the size distribution is located at 8.3 nm), do not indicate any aggregation and are quite uniformly dispersed on the surface of the alumina support. The Pd(0) particles obtained on the Al₂O₃-Fe₂O₃ support (Fig. 9a) are slightly larger (the average size is 8.8 nm). However, most of them are aggregates composed of several discernible particles in guasispherical arrangements. For both of the supports the Pd(0) size distributions are practically symmetric with FWHM of 4.3 and 4.8 nm, respectively. In both cases Pd(0) nanoparticles recovered after the Heck reaction were practically the same as the freshly prepared and no redispersion of the Pd(0) nanoparticles was observed. Contrastingly, in the Heck reaction carried out in molten [ⁿBu₄N]Br the change of the size of alumina-supported Pd(0) particles was very significant [26]. This fact suggests that under the conditions chosen in this work the process is more heterogeneous, although participation of soluble palladium forms cannot be ruled out.

Pd(0) nanoparticles are also formed in situ from the supported Pd(II) precursors under the Heck reaction conditions. Thus obtained particles are generally several nanometers larger (especially in case of the Al_2O_3 -Fe₂O₃ support) when compared to the Pd(0) catalysts prepared by reduction with N₂H₄·H₂O (Table 5). However, not only is the average nanoparticle diameter larger but also there are some more significant morphological differences. Pd(0) nanoparticles obtained from the supported Pd(II) precursors (Figs. 8b and 9b) are mostly characterized by very well defined geometrical shapes with many corners and edges. Comparing to the Pd(0) catalysts, it is clear from the histograms that the size distributions are also broader, with less defined maxima and somewhat asymmetric, shifted towards larger particles. Analogous effect is also observed for the Pd catalysts supported on the Al₂O₃-CeO₂ mixed oxide.

4. Conclusions

Palladium catalysts supported on the alumina-based mixed oxides have been used in the Heck reaction leading to mono- and diarylated olefins. Their catalytic activity in the cross-coupling of aryl halides with cinnamic ester or aldehyde is similar to that reported for homogeneous systems with phosphane or tetraalkylammonium salt co-catalysts. Good-to-excellent yields of the coupling products were obtained in 4h, without any additives. As confirmed by TEM studies, the supported Pd(II) was reduced to Pd(0) during reaction forming nanoparticles that probably act as catalytically active species. Although participation of soluble palladium forms in the catalytic process cannot be excluded, recyclability of the investigated systems was confirmed. Higher palladium leaching was observed for Pd(II) than in case of the immobilized Pd(0) catalysts, which often consist of nanoparticles that are sterically constrained in the pores of the support [60]. The high level of Pd leaching allows to predict that the catalysts studied are not suitable for longer uses.

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