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Supported palladium as catalyst for carbon–carbon bond construction (Heck reaction) in organic synthesis

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Abstract

The catalytic activity and selectivity of palladium supported on various metal oxides and zeolites in carbon–carbon coupling reactions of aryl bromides with olefins (Heck reaction) are reported and reviewed. The supported Pd particles and entrapped Pd complexes exhibit high activity towards the Heck reaction for very small palladium concentrations (0.1 mol%). The activity is determined by the nature of the support and the Pd dispersion. The electronic nature of the aryl bromides and the olefins has a dominating effect on the reaction yield. The catalysts can be easily separated from the reaction mixture and reused after washing without loss in activity. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic carbon–carbon coupling reactions are of considerable interest for the production of fine chemicals. The olefination of aryl halides (Heck reaction), one of the most important CC coupling reactions in organic synthesis [1–3], is mostly catalyzed by palladium complexes in homogeneous solution. Important advantages of this reaction are the broad availability of aryl bromides and chlorides, and the tolerance of the reaction for a wide variety of functional groups. In the last years, the development of new highly active Pd complexes allowed the activation and conversion to considerable extent of even aryl chlorides [4–6], which are less reactive than bromides and iodides. Regarding industrial applications, however, these catalysts are expensive (Pd, phosphanes or special ligand systems) and only very few experiments are reported about the separation from the reaction mixture and their reuse [7,8]. In addition to the separation problems, often deactivation of the homogenous catalysts by formation of less active or inactive colloidal Pd species is encountered at the comparatively high reaction temperature.

The problems concerning thermal stability (high reaction temperatures), separation and recovery of the Pd complexes were tried to overcome by the use of heterogeneous palladium systems. Polymer-supported Pd complexes were used for the activation of aryl iodides by several groups. For the conversion of aryl chlorides and bromides, Pd on carbon [9,10], on metal oxides [11–13] and zeolites [14,15] were found to be suitable catalysts. Stabilized Pd colloids [16–19] can catalyze the Heck reaction of aryl iodides (and partially bromides).

The conversion of aryl chlorides by the heterogeneous catalysts Pd/C and Pd/MgO was achieved under

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rather special conditions [9–11]. In different papers, an influence of the support on the activity and in some cases on the selectivity of the Heck reaction were observed [20–22]. These investigations concerned in particular the reaction of butylvinyl ether with substituted benzoyl chlorides [20–22] and the olefination of aryl iodides [23,24]. Reactions of different aryl bromides with substituted alkenes have been catalyzed by Pd supported on mesoporous silica [12], metal oxides [13], zeolites [14,15] and carbon [25]. The clearly increasing number of papers concerning the heterogeneously catalyzed Heck reaction reflects the efforts to solve the problems discussed above and also to understand the mechanism of this reaction. Recent reports focus on or at least describe investigations of the leaching phenomenon, which is important to realize the actually active species and to manage complete separation of Pd [25]. Some papers deal with the influence of the structure of the Pd surface (structure–activity relationships) [18–22], others ask whether the heterogeneous reaction is catalyzed homogeneously or heterogeneously.

Concerning the last question, there are contradictory ideas concerning the mechanism and structure–activity relationships in the heterogeneous Heck reaction up to now. Based on model reactions (hydrogenations), a surface mechanism and the structure of the active centers were derived involving highly unsaturated Pd atoms on the surface of Pd particles [18,20–22]. However, also the idea that soluble palladium complexes (leaching) are the only active species in the Heck reaction is proposed [25,26]. Other investigations could correlate the Pd dispersion and activity (conversion, reaction yield) [13]. The latter idea is underlined by the very high activity of Pd complexes grafted on metal oxides or entrapped into zeolite cages [15]. Very recent studies demonstrate that for phosphane or ligand-free Pd catalyst systems based on simple Pd salts in situ formed, few nanometer small palladium colloids act as catalyst in the Heck reaction [19]. In general, however, it seems to be not yet clear, whether the Heck reaction catalyzed by supported Pd proceeds according to a homogeneous (resolved Pd species) or a heterogeneous mechanism. It has to be taken into account thereby that the reaction under consideration represents a very complex system (a base is needed, a salt is formed and precipitated) working under rather extreme conditions (temperatures around 140°C for the reaction of aryl bromides) and that different reactions and conditions can occur according to different mechanisms.

The present paper summarizes for the first time investigations on the Heck reaction of the broadly available aryl bromides with olefins catalyzed by palladium supported on a broad variety of different oxide and zeolite supports. These catalysts can easily be prepared or are partially even commercially available. The results (activity, selectivity, influence of substituents and reaction conditions, preparation, Pd dispersion, separation and reuse) are compared to each other and to the literature. Mechanistic aspects are discussed.

2. Experimental

2.1. Preparation of the catalysts

The (oxide) supports were prepared according to literature procedures or supplied by Degussa-Hüls AG (TiO_2 P25, ZrO_2 and SiO_2 Aerosil 200), Hoechst AG (Pd/C) and Fluka (Pd/Al_2O_3) (Table 1). The zeolites were purchased from Sigma–Aldrich Chemical (LZ-Z-52) and by Degussa-Hüls AG (Table 1).

A solution of $Pd(acac)_2$ in benzene (made from 143.1 mg of $Pd(acac)_2$ in 15 ml of benzene) was added to 1 g of oxide support. The mixture was stirred for 1 h at room temperature before the benzene was evaporated to give a slightly yellow solid. This was reduced under hydrogen flow (150 ml min^{-1}) in a U-tube reactor at 70, 250, 400 or 600°C for 2 h to give the desired Pd/MO_x catalyst as a gray material. Typical procedures for the preparation of Pd/zeolite catalysts by ion exchange with aqueous solutions of $[Pd(NH_3)_4]^{2+}$ [14] or for Pd complexes entrapped in zeolite cages [15] as well as the following treatment are reported in the literature.

2.2. Test of the catalytic activity

The preparations and manipulations were performed under ambient atmosphere. The catalytic reactions were carried out in pressure tubes after purging with argon. The qualitative and quantitative analysis of the reactants and the products was made by gas liquid chromatography (GLC). Conversion and selectivity are represented by product distributions

Table 1
Origin and analytical data of the supports

Support	Origin/preparation	Specific surface area (BET) (m^2/g)	Pd content (wt.%)[a]
MgO I	[27]	65	1.0 or 4.9
TiO_2 I	[28]	113	1.0 or 4.3
TiO_2 II	P25 (Degussa-Hüls AG)	49	4.3–4.6
SiO_2	Aerosil 200 (Degussa-Hüls AG)	189	1.1 or 4.3
ZnO	[29]	45	4.5
Al_2O_3	Fluka AG	198	5.0
ZrO_2	Degussa-Hüls AG	39	5.5
C	Hoechst AG	915	5.0
H-mordenite	Degussa-Hüls AG		7.0
H-Y	Sigma–Aldrich		6.8
Na-Y	Sigma–Aldrich		1.1[b]

[a] Determined by AAS.
[b] Complex $[Pd(NH_3)_4]^{2+}$ entrapped into the zeolite supercage.

(=relative area of GLC signals) and GLC yields (=relative area of GLC signals referred to an internal standard calibrated to the corresponding pure compound, ($\Delta_{rel} < \pm 10\%$)).

2.3. General procedure for the catalytic tests

10 mmol of bromobenzene (aryl bromide), 15 mmol of styrene (alkene), 15 mmol of NaOAc and 0.1 mol% of Pd (as heterogeneous catalysts) were introduced in a pressure tube. 10 ml of solvent (DMAc p.a.) were added and the mixture was de-aerated by an argon flow for 5 min. The reactor was then placed in a preheated oil bath at 140°C for 20 h with vigorous stirring and after cooling to room temperature the reaction mixture was analyzed by GLC.

For the recycling studies, the catalyst was separated from the reaction mixture, washed with CH_2Cl_2 in order to remove adsorbed organic substrates, dried at room temperature and reused without any further treatment.

2.4. GLC analysis

A homogeneous 3 ml sample of the reaction mixture was sampled and quenched with 3 ml of water in a test tube. The mixture was extracted with 2 ml of CH_2Cl_2, the organic layer was filtered and dried over $MgSO_4$. The resulting dry organic layer was then analyzed by GLC.

2.5. Purification of the *trans*-stilbene product **3** (for the selected model reaction)

After the separation of the heterogeneous catalyst, the reaction phase was added to CH_2Cl_2 (50 ml) and washed with H_2O (3×15 ml). The organic layer was separated, dried over $MgSO_4$ and then evaporated. The residue was dissolved in 15 ml of CH_2Cl_2 and pentane (8 ml) was added. The solution was cooled to −18°C to give the *trans*-stilbene **3**, which was collected by filtration. The mother liquor was concentrated, treated as the original liquor to give additional product. The purity of the product was estimated by GLC to be >99.8%.

Analytical data: m.p.: 118°C — white plates. ^1H NMR: $CdCl_3$, 400.13 MHz: 7.64 (d, $^3J = 7.0$ Hz, 4H, *ortho*-vinyl-C_6H_5); 7.48 (pseudo-t, $^3J = 7.5$ Hz, 4H, *meta*-vinyl-C_6H_5); 7.39 (pseudo-t, $^3J = 7.0$ Hz, 2H, *para*-vinyl-C_6H_5); 7.24 (s, 2H, CH-vinyl). ^{13}C NMR: $CdCl_3$, 400.13 MHz: 137.28 (C-vinyl-C_6H_5); 128.63 (*meta*-vinyl-C_6H_5); 128.48 (CH-vinylic); 127.56 (*para*-vinyl-C_6H_5); 126.48 (*ortho*-vinyl-C_6H_5). $C_{14}H_{12}$ — elemental analysis: Found (calc.): C 92.01 (93.29), H 6.64 (6.71).

2.6. Methods

NMR spectra of the organic products were recorded with a Bruker AM 400 spectrometer (^1H NMR were referenced to the residual protio-solvent: $CdCl_3$, $\delta = 7.25$ ppm; ^{13}C NMR were referenced to the C signal of the deutero-solvent: $CdCl_3$, $\delta = 77$ ppm). GLC were performed on a chromatograph HP 6890 series equipped with an FID detector and a HP-1 column (cross-linked methylsiloxane, 30 m × 0.25 mm × 0.25 mm film thickness). The absolute palladium content of the catalysts and of the supernatant solution (after reaction) was determined by atomic absorption spectroscopy (AAS).

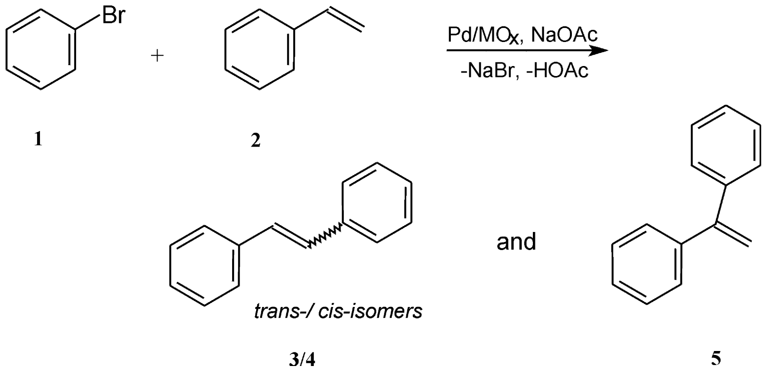
H_2 chemisorption measurements were performed after in situ reduction in hydrogen at the given temperature (70, 250, 400 or 600°C) by a Quantachrome Autosorb Automated Gas Sorption System (Quantachrome Corporation). Electron microscopy (TEM) was carried out on a Jeol 100CX microscope with an instrumental magnification of 100 000× and an acceleration voltage of 100 kV. For the measurements, the dry catalyst samples were deposited on a carbon (copper) lattice without solvent.

3. Results and discussion

For most of the following investigations in particular for the deduction of structure–activity relationships, we have chosen the reaction of bromobenzene with styrene as a model reaction (Scheme 1). This reaction gives reasonable yields of Heck product, thereby allowing the observation of small changes in the activity of the catalysts. In addition, the influence of different functional groups of the aryl bromide and of the nature of the alkene were studied. The supported Pd catalysts (Table 1) were prepared according to standard procedures: Pd on metal oxides by impregnation, Pd on zeolites by ion exchange (see Section 2). Palladium loadings of 1 or 5 wt.% were used, whereby the total Pd concentration in the Heck experiments was always very low, only 0.1 mol% (0.2 mol% for the Pd/zeolite catalysts) Pd relative to the aryl bromide were used. The higher Pd loadings (5 wt.%) were used to get expressive analytical results concerning particle size and dispersion (H_2 adsorption and transmission electron microscopy). The catalysts were thermally (pre)treated in different ways in order to investigate the influence of dispersion and oxidation state of palladium. The Pd/zeolites investigated involve Pd particles as well as molecular Pd complexes entrapped into zeolite cages. This should allow to estimate the influence of the Pd dispersion on the activity of the heterogeneous catalysts.

3.1. Catalytic properties (conversion and selectivity) in the model reaction

The conversion and selectivity of selected Pd/MO_x and Pd/zeolite catalysts in the reaction of bromobenzene with styrene (Scheme 1) obtained by GLC are compared in Table 2. Most of supported Pd catalysts exhibit high activity and selectivity in the Heck reaction of the non-activated bromobenzene with styrene (Scheme 1) for very low Pd concentrations of 0.1 mol%. *trans*-stilbene is observed as the main product in all cases.



Scheme 1. Heck reaction of bromobenzene with styrene catalyzed by Pd/MO_x.

Table 2
Catalytic activity and selectivity of palladium supported on different oxides and zeolites

Catalyst (5 wt.%)	Conversion (%)[a]	1,1-Diphenylethene **5** (%)[a]	*cis*-stilbene **4** (%)[a]	*trans*-stilbene **3** (%)[a]
Pd/MgO	39.7	2.9	0.3	36.5
Pd/TiO_2 I	41.2	3.0	0.4	37.9
Pd/TiO_2 II	45.9	3.3	0.4	42.2
Pd/SiO_2	8.2	0.6	0.1	7.5
Pd/ZnO	33.3	2.6	0.3	30.3
Pd/ZrO_2[b]	49.1	3.7	0.4	45.0
Pd/C	83.8	6.4	0.8	76.6
Pd/H-mordenite	82.5	6.0	0.7	71.5
$[Pd(NH_3)_4]$/NaY	100	6.5	0.7	84.9

[a] GLC yields ($\Delta_{rel} < \pm 10\%$); reaction conditions: 10 mmol bromobenzene, 15 mmol styrene, 12 mmol sodium acetate, 10 ml DMAc, 0.1 mol% Pd/MO_x catalyst (5 wt.%), diethyleneglycol dibutylether as internal standard at 140°C for 20 h.

[b] Reduced at 250°C.

The selectivity is very similar for all catalysts (*trans*-stilbene:*cis*-stilbene:1,1-diphenylethane = 92: 1:7) and comparable to typical homogeneous systems (e.g. palladium acetate + 5 eq. $P(C_6H_5)_3$) [1,2]. The activation of aryl chlorides as described by Julia and Duteil [9], Julia et al. [10] and Kaneda et al. [11] was not possible under the reaction conditions used by us (see, however, also Table 3). The only exclusion was the very active complex $[Pd(NH_3)_4]^{2+}$ entrapped in zeolite Y, which couples styrene and chloroacetophenone to ca. 50% at 170°C (about 8% dehalogenation product).

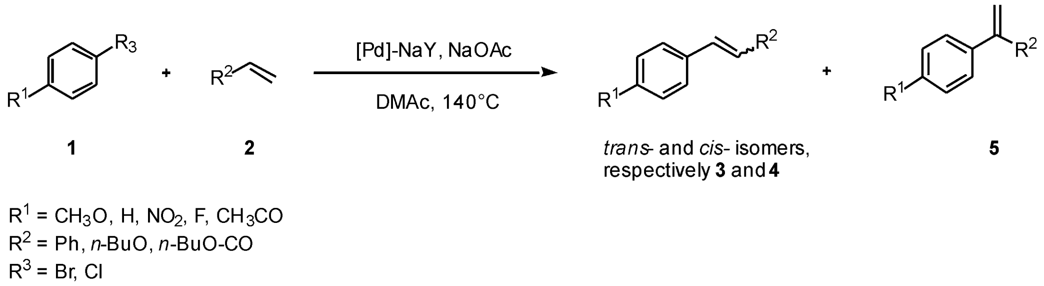
3.2. Influence of functional groups and of the nature of the alkene

Besides styrene, e.g. the alkenes butylacrylate and ethene can be converted, however, with lower yields than for styrene (Scheme 2, Table 3). As expected, electron-poor olefins gave the better yields than electron-rich ones. Generally, the gradation of the aryl bromide conversion is similar to homogeneous catalysis. It depends on the activation of the aryl bromides by an electron withdrawing substituent in *para*-position to the bromine and the electron density

Table 3
Catalytic activity and selectivity of palladium supported on different oxides and zeolites for different substituents of aryl bromide and alkene (Scheme 2) [13,15,30]

Catalyst	Substituents (Scheme 2) R^1; R^2; R^3	Conversion (%)[a]	Yield (main product, %)[a]
Pd/TiO_2 (1 wt.%)	H; $OCO(CH_2)_4H$; Br	40	39
Pd/MgO (1 wt.%)	H; $OCO(CH_2)_4H$; Br	28	25
Pd/ZrO_2 (1 wt.%)	H; $OCO(CH_2)_4H$; Br	41	40
Pd/ZrO_2 (1 wt.%)	H; H; Br	27	18
Pd/MgO (1 wt.%)	CH_3CO; C_6H_5; Cl	39	10
Pd/MgO (1 wt.%)	H; C_6H_5; Br	50	49
Pd/MgO (1 wt.%)	F; C_6H_5; Br	87	87
Pd/MgO (1 wt.%)	CH_3CO; C_6H_5; Br	100	100
Pd/MgO (1 wt.%)	NO_2; C_6H_5; Br	100	100
$[Pd(NH_3)_4]^{2+}$/NaY	H; CH_3O–CO; Br	99	91
$[Pd(NH_3)_4]^{2+}$/NaY	CH_3O; C_6H_5; Br	100	81
$[Pd(NH_3)_4]^{2+}$/NaY	H; C_6H_5; Br	95	85
$[Pd(NH_3)_4]^{2+}$/NaY	F; C_6H_5; Br	100	93
$[Pd(NH_3)_4]^{2+}$/NaY	NO_2; C_6H_5; Br	100	95

[a] GLC yields ($\Delta_{rel} < \pm 10\%$); reaction conditions: 10 mmol aryl bromide, 15 mmol alkene, 12 mmol sodium acetate, 10 ml DMAc, 0.1 mol% Pd/MO_x catalyst (1 or 5 wt.%), diethyleneglycol dibutylether as internal standard at 140°C for 20 h (rounded values).



Scheme 2. Heck reaction of substituted aryl bromides with alkenes catalyzed by supported palladium.

of the olefin π-bond. Actually, the aryl bromides with electron withdrawing groups (R = F, NO_2, CH_3CO, Table 3) show complete turnover already after few hours [14,15,30]. Very similar to the results of Table 2, a strong influence of the support is observed (see below).

3.3. Influence of the support

Selected data of the catalyst supports are summarized in Table 1. For TiO_2 and MgO, more than one support was prepared and used for Pd immobilization in order to get an impression on the influence of different support surface areas or modifications. These experiments show that the main influence of the support is based on its chemical nature and that the reproducibility of this support influence in the Heck reaction is satisfactory. Whereas the reaction selectivity is practically not influenced by the catalyst, the activity is dominated by the support. Roughly, the following order of the supports can be derived concerning the activity for olefination of bromobenzene with styrene (conversion):

$$(C >)TiO_2 > ZrO_2 > MgO > ZnO > SiO_2$$

This corresponds to the (more extensive) series found for oxide-supported catalysts with 1 wt.% loading [30] (no significant influence of the Pd loading).

Comparable experiments concerning the Heck reaction of bromobenzene with styrene are reported in the literature for supported Pd on mesoporous silica [12] and zeolites [14,15]. With mesoporous silica as support, 39% conversion was achieved only at 170°C and after 48 h reaction time. This comparatively low activity (despite high Pd dispersion and sophisticated preparation techniques) is obviously due to the silica support (conversion of bromobenzene (mol) per total Pd content (mol) ("TON"): 200 [12], 180 for SiO_2 (at 140°C) and 640 for TiO_2 [13]) and fits the order obtained in this paper very well.

The Pd-exchanged zeolites exhibit an even higher activity (more than 80% yield of *trans*-stilbene after 20 h at 140°C, Table 2), possibly due to the stabilization of a high Pd dispersion (small Pd clusters or Pd complexes, see below) and additional effects (e.g. water) [14,15]. The most active heterogeneous system is found to be $[Pd(NH_3)_4]^{2+}$ entrapped into zeolite NaY, which can convert even activated aryl chlorides (at higher temperatures). The Pd loading (4–7 wt.%), the zeolite structure (mordenite or Y-type) and the zeolite counter ion (H- or Na-form) show only a minor influence on the conversion and selectivity in the Heck model reactions investigated [14] (data not shown).

In the literature, the influence of the support is attributed or reduced to its acidity or basicity [11,20–24]. Generally, Pd on basic supports is found to be more suitable for the activation of aryl halides [11,23,24], whereas for benzoyl chlorides acidic supports seem to give the best results [20–22]. Obviously, this does not fit at least the acidic properties of the reducible transition metal oxides (TiO_2 and ZrO_2) in the above series. However, this problem has many correlated facets, which have to be taken into account. One of this is the correlation of the nature of the support and the Pd dispersion (see below).

3.4. Influence of the palladium surface area (dispersion)

Table 4 represents chosen data of the catalytic tests in comparison to the corresponding Pd surface area

Table 4
Correlation between catalytic activity (yield) in the reaction of bromobenzene with styrene and the specific Pd surface areas of Pd/MO_x catalysts for different reduction temperatures (Scheme 1)

Catalyst (5 wt.%)	Reduction temperature (°C)	Yield (%)	Specific Pd surface area (m^2/g)
Pd/TiO_2	250	51	1.42
	400	59	0.63
	600	47	0.06
Pd/MgO	70	37	0.85
Pd/MgO	400	16	0.15
Pd/SiO_2	70	8	1.20
Pd/C	70	84	4.29

(dispersion, obtained by H_2 adsorption measurements [13]) for different supports and reduction temperatures. The expected decrease of the Pd dispersion with increasing reduction temperature (from 70 to 400°C) is observed for MgO and is connected with a corresponding decrease in catalytic activity (Table 4). For MgO we can state: the higher the Pd dispersion (the lower the reduction temperature), the higher is the activity.

The opposite is observed for Pd on titania. By increasing the reduction temperature from 70 to 400°C, the dispersion deduced from hydrogen adsorption measurements decreases, but the activity increased. Only after reduction at 600°C, both Pd (support) surface area and activity decreased (Table 4).

Summarizing the results represented in Table 4 there seem to exist supports which behave as inert concerning the Heck reaction. These are SiO_2 and carbon. The activity is then roughly correlated to the Pd surface area (factor ≈4 between SiO_2 and Carbon, Table 4). Compared to these supports there are catalysts, the activity of which is clearly higher than expected from their Pd dispersion. This is, e.g. MgO, i.e. a typical basic support. We cannot exclude that the support itself takes part in the reaction (acting as base [23,24]). There is a third group of supports for Pd, TiO_2 (and possibly other reducible oxides) — one of the most active systems in the above oxide series — where a reverse correlation is found between activity and Pd surface area (below 600°C). Titania is well known for comparable effects of the reduction temperature (around 450°C) on the activity in several gas phase reactions. The effect called SMSI (strong metal–support interactions) is explained by the partial coverage of the noble metal surface by (reduced) titanium oxide species [31]. The observations were confirmed by TEM and XRD measurements. A series of TEM figures were taken from Pd/MgO for two different reduction temperatures ($T = 70$°C: mean diameter, $d = 9.7$ nm; $T = 400$°C: $d = 13.9$ nm), for Pd/TiO_2 after reduction at 250°C ($d = 7.7$ nm) and of the same Pd/TiO_2 catalyst after use in the Heck reaction ($d = 4.6$ nm). The result of statistical analyses [13] yields the mean particle diameters given in parentheses above. For TiO_2 the number of Pd particles included in the analysis was lower, the particle diameters should be taken as estimations. The particle sizes deduced from TEM (and XRD [13]) are generally smaller (one-half or even less) than those calculated from the hydrogen chemisorption measurements. Possibly not all Pd surface atoms chemisorb hydrogen (are reduced to Pd(0)). The order of the particle sizes/surface area are, however, in all cases in qualitative agreement for both methods.

Pd dispersion after reaction. Structural changes of the heterogeneous catalysts during or after reaction are important aspects for a better understanding of structure–activity relationships in this reaction. They were never regarded for heterogeneous Heck reactions in the literature up to now. It is problematic to do this, because the mass of the solid increases during the reaction: after separation of the liquid solution, the remaining solid consists of the Pd/MO_x catalyst, residual base, the stoichiometric amount of the salt (NaBr) and sometimes partially insoluble products. That is why, before the TEM pictures were taken, one used catalyst Pd/TiO_2 (250°C) was first washed with dichloromethane (removal of organic components) and then with water (removal of the salts) and dried in air. The estimation of the mean Pd particle

Table 5
Recycling and reuse of selected Pd/MO_x catalysts in the Heck reaction of bromobenzene with styrene (Scheme 1), conversions (%)[a]

Catalyst (1 wt.%)	Recycling					
	0	1	2	3	4	5
Pd/MgO	49	27	96	8	61	4
Pd/TiO_2	47	37	66	18	54	19
Pd/Al_2O_3	42	49	98	7	60	7
Pd/SiO_2	17	33	79	15	69	41

[a] GLC yields ($\Delta_{rel} < \pm 10\%$); reaction conditions: 10 mmol bromobenzene, 15 mmol styrene, 12 mmol sodium acetate, 10 ml DMAc, 0.1 mol% Pd/MO_x catalyst (5 wt.%), diethyleneglycol dibutylether as internal standard at 140°C for 20 h (rounded values).

diameter after the reaction by TEM measurements yields a slight reduction of the particle size during the Heck reaction. This indicates some mobility of the palladium under reaction conditions ($T = 140°C$) and a corresponding restructuring of the Pd on the surface of the solid(s). The trials to determine the Pd dispersion by H_2 chemisorption experiments were not successful. No hydrogen uptake could be measured for the used catalyst before washing [13].

3.5. Separation, recycling and reuse

These tests were connected to the question, whether the supported Pd catalysts show the advantages of a heterogeneous reaction. In fact, in chosen experiments the catalysts were reused for a second run in the same reaction under identical condition after separation from the reaction mixture of the initial run and washing with CH_2Cl_2 (see Section 2). In general, the recycled catalysts (Pd/TiO_2, Pd/MgO, Pd/Al_2O_3, Pd/SiO_2) showed high activity as in the first run (Table 5) and even an increased activity in particular after two runs. From the experimental point of view it has to be mentioned that the handling of the increasing mass of the solid (catalyst + base + salt) becomes more difficult for every run, what reduces the reproducibility. Additional washing with water after separation (after the third run, right of the fat line in Table 5) remarkably reduces the activity of the catalysts. Further runs without contact with water increase the catalyst activity again, before it breaks down after additional recyclings. More detailed investigations are necessary and in progress in order to understand and overcome these effects [30].

3.6. Residual catalytic activity in solution after separation of the solid catalyst (leaching)

Probing experiments were performed to estimate the contribution of Pd leached into solution to the catalytic activity. The organic phase of a first run was separated from the solids after 2 h reaction time. Additional base (12 mmol sodium acetate) was added to the clear filtrate, and the composition of the reaction mixture was determined by GLC before and after continuing the reaction for 20 h at 140°C. The differences found between the two GLC determinations give a qualitative information about residual, catalytically active palladium (supported or resolved as complexes) in solution after catalyst separation. The results for Pd/MgO show that some Pd (or catalyst) was not separated from solution by filtration [30]. This residual activity, however, cannot explain the high conversion of the complete catalytic system (separated solid catalyst + Pd in solution). In fact, there are indications that at least a remarkable percentage of the residual activity is due to Pd on small support particles, which passed through the filter. The use of two filters and special filter combinations (Whatman + cellulose nitrate) can reduce the residual activity of the filtrate to a minimum: the yield was reduced with two filters to 20% and with the filter combination to less than 6%. The absolute Pd content in the supernatant solution after filtration at the end of the reaction (determined by AAS) amounts to few ppm only. This corresponds to few percent or sometimes even less than 1% of the total Pd of the catalyst. This leached Pd amount depends on several variables (see also [25,30]), which are the subject of current investigations.

Summarizing the experimental results the question arises, whether the reactions studied proceed according to a homogeneous or heterogeneous mechanism. It has been mentioned that contradictory models were reported: based on model reactions (hydrogenations), a surface mechanism and the structure of the active centers were reported involving highly unsaturated Pd atoms on the surface of Pd particles [18,20–22]. However, also the idea that soluble palladium complexes (leaching) are the only active species in the Heck reaction is proposed [25,26]. From the results presented in this paper, it can at least be concluded that there are clear indications for relationships between the structure or texture of the supported palladium catalysts and their activity in the Heck reaction studied. These arguments are the clear and reproducible influence of the nature of the support and of the Pd surface area (dispersion). There are reasonable explanations for at least some of the support effects, however, many additional possibilities have to be taken into account. These are, e.g. that different Pd dispersions could be determined by the different supports, the possible participation (resolution) of basic supports in this specific reaction [23,24] (HBr is an intermediate product of the Heck reaction) or the influence of electronic properties of the oxide and strength of the Pd–support interactions.

The arguments require a heterogeneous surface mechanism, i.e. they pre-suppose that resolution, re-precipitation and re-dispersion of the Pd during the reaction can be neglected. Although the influence of the support and Pd dispersion, the recycling and re-usability of the catalysts and the high activity compared to colloids indicate such a surface mechanism, it is not an evidence, and there are also arguments [25,26] for analogies to homogeneous Heck catalysis. The observed residual activity of the solution after separation of the solid (leaching), restructuring of the Pd on the surface under reaction conditions and the identical selectivity of the Heck reaction catalyzed by homogeneous (Pd complexes) and supported metal particles have to be mentioned in this context. Further studies are necessary to clarify this problem.

4. Conclusions

Palladium supported on metal oxides and zeolites exhibits high activity and selectivity in the formation of carbon–carbon bonds by arylation of olefins (Heck reaction). Analogous to homogeneous Heck catalysis the gradation of the aryl bromide conversion depends on the activation of the aryl bromide by an electron withdrawing substituent in *para*-position to the bromine and the electron density of the olefin π-bond. Activated aryl bromides show complete turnover at 140°C after few hours using the heterogeneous catalysts. Selected Pd/MO$_x$ and Pd/zeolite systems presented here are the most active heterogeneous catalysts for the activation of aryl bromides reported in the literature up to now. The reaction can be performed with catalysts, which are easily prepared or commercially available without additional ligands (phosphanes). The activity of the catalysts can be correlated with the nature of the support and the palladium dispersion. For supports being “inert” with respect to the Heck reaction (SiO_2, carbon), the activity (conversion, yield) is directly connected to the Pd surface area. A second group of catalysts shows a higher activity than expected from their Pd dispersion (MgO and other basic oxides). Pd on TiO_2 (transition metal oxides) shows a reverse correlation between activity and Pd surface area (below reduction temperatures of 600°C). The catalysts can be recycled and reused without loss but even with an increase in activity. The observed residual activity of the homogeneous solution after separation of the solid catalyst is found to be dependent on the filtration procedure. Although there are several indications for a heterogeneous reaction mechanism, the participation of resolved Pd species (colloids or complexes) cannot be excluded.

The facts that no inert atmosphere and no ligands are necessary, the easy separation, the potential to control and increase the catalyst activity and the easy availability makes the supported Pd catalysts to an interesting alternative to homogeneous catalysts for industrial applications.

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