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Palladium/Magnesium-Lanthanum Mixed Oxide Catalyst in the Heck Reaction

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Abstract: A new, reusable palladium/magnesium-lanthanum mixed oxide catalyst has been found to exhibit unprecedented high catalytic activity and selectivity for the heterogeneous Heck cross-coupling reaction of aryl halides with alkenes. The nature of the aryl halides has a determinate effect on the reaction yield. The corresponding reactions of a wide range of activated and non-activated aryl bromides and chlorides furnished the arylated product with high *E/Z* isomer ratios even already at 80 °C. The stereoselectivity depended on the nature of the olefins.

Keywords: catalyst recycling; Heck reaction; magnesium-lanthanum mixed oxide; palladium

Introduction

The palladium-catalyzed coupling of terminal olefins with aryl and vinyl halides (the Heck reaction) is an important reaction thanks to its high tolerance of functional groups and its general applicability.[1–3] The arylalkenes obtained are used as intermediates for the synthesis of biologically active compounds,[4,5] natural products,[6] or as precursors of conjugated polymers.[7] This reaction has also been used in the pharmaceutical industry for the production of compounds such as naproxen or octyl methoxycinnamate.[8]

The Heck reaction commonly proceeds in the presence of homogeneous palladium catalysts, generated from either palladium(0) compounds such as, e.g., $Pd(PPh_3)_4$ and $Pd_2(dba)_3$, or palladium(II) salts, such as acetate and chloride.[9] Several ligands such as phosphines, phosphites, carbenes, or thioethers have been successfully employed for this reaction.[1–3,10,11] However, the homogeneous catalysis creates problems for recovery and reuse and might result in palladium contamination of the product. On the other hand, the use of phosphines, which are commonly used as electron-donating ligands in the catalysts, is undesirable because they are toxic and air-, as well as moisture-sensitive. Moreover, under Heck reaction conditions both the phosphines and their palladium complexes are prone to decomposition so that excesses of phosphine and palladium are required. The excess of phosphine reduces the reaction rate while the higher amount of palladium increases the cost of the process.[10]

Heterogeneous catalysis could solve some of these problems. The catalysts could be recovered from the reaction mixture by simple filtration, and then reused. In recent years a number of reports have appeared about the heterogeneous Heck reaction catalyzed by supported palladium catalysts such as palladium on charcoal,[12] palladium on magnesium oxide,[13] palladium on simple oxides such as silica,[14] alumina or titania,[14,15] palladium/Nb-MCM-41,[14] palladium/polymeric materials,[16] palladium/zeolites.[17–21] These supports have a common feature: they are neutral or solid acids. A few reports relate to the use of basic supports such as LDH,[22] basic zeolites[23] or alkali-exchanged sepiolite,[24] which are weak bases.

From earlier works the support is known to affect the electronic density at the surface of palladium and platinum atoms, their solubility in aqueous nitric acid, and their catalytic properties for dechlorination. Whereas acid supports behave as electron acceptors, basic supports have been demonstrated to behave as electron donors relative to palladium[25] or platinum.[26] The electron donation was measured by the shift of the infrared band of CO at low coverage. The CO band shifted toward higher frequencies on the supports which possessed acid sites and towards lower frequencies on basic supports such as magnesium oxide or basic zeolites. The shift of CO between an acid and a weakly basic support reaches 100 cm^{-1} for palladium and 50 cm^{-1} for platinum. Due to this electron donation the support can play the role of phosphines in homogeneous complexes. Indeed, Choudary et al.[27] have already reported the immobilization of nanocrystallites of palladium on layered double hydroxide, which was highly active in non-aqueous ionic liquid media and microwave conditions for the Heck reaction. Palladium on basic zeolites has recently been reported to exhibit, for Heck coupling, an increase of activity compared to acid zeolites and is related to the basicity of the support.[23]

The metal-support interaction has also been observed to play a role on the rate of dissolution or sulfation of platinum on different supports. The rate of platinum dissolution increased on acid supports,[28] and the negatively charged platinum, formed on hydrotalcite as support was less resistant to sulfur than neutral platinum particles.[26] The catalytic properties of palladium for the dechlorination of CF_2Cl_2 have been found to be very sensitive to the choice of the support: acid supports favor dechlorination which was inhibited on basic oxides. The kinetic study suggested that the selectivity was controlled by the bond strength between a carbene-like species, CF_2, and the surface. The strength of this interaction was supposed to vary with the electron availability at the palladium surface, in good agreement with the shift of the IR CO band for palladium/Al_2O_3 and palladium/AlF_3.[29] Both dechlorination of CF_2Cl_2 and Heck reactions involve the oxidative addition of a chlorinated compound at the palladium atom, and strongly basic supports are expected to behave differently from zeolites in different aspects. In a recent work, Srivastava et al.[30] measured the amount of palladium leached into the solution during the reaction. After a significant initial leaching, palladium was trapped onto the SAPO-31 support at the end of the reaction. SAPO-31, similar to zeolites or carbon, is an acid support and a cation exchanger, and this experiment suggests that palladium leaches as the cation. Basic supports are anion exchangers, so that this type of redeposition is excluded, and it is therefore interesting to check recycling in such a case.

Magnesium-lanthanum mixed oxide (MgLaO) appears to be a stronger base than hydrotalcite or fluorides[31] showing for the Michael addition the same catalytic properties as the proazaphosphatranes described by Kisanga et al.[32] In this report, we present the preparation and characterization of a new palladium/magnesium-lanthanum mixed oxide catalyst (Pd/MgLaO) and the examination of the catalytic properties, in the Heck reaction, of this type of catalyst that does not require an inert atmosphere, is thermally stable, can be easily handled and reused.

Results and Discussion

Preparation of Palladium/Magnesium-Lanthanum Mixed Oxide

The magnesium-lanthanum mixed oxide was prepared by the co-precipitation method described earlier.[31] It contained 39.8% La, 5.4% K and 37% H_2O. The powder XRD pattern of the uncalcined mixed oxide showed the diffraction lines of a hydrated lanthanum carbonate and of magnesium and lanthanum hydroxides with parameters corresponding to those reported in the literature.[31] This triphasic solid probably consisted of a layer of lanthanum oxide deposited on magnesia. This mixed oxide is macroporous and shows a surface area of 37.6 m^2/g after calcination at 923 K.

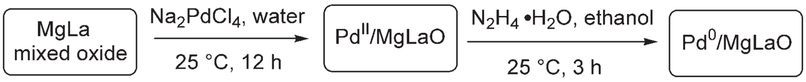
The palladium(II)/magnesium-lanthanum mixed oxide was prepared by ion exchange, using an aqueous solution of sodium tetrachloropalladate(II), followed by washing. Using this procedure, highly dispersed chloropalladate anions are fixed at the surface. Among the preparations of palladium nanoparticles, the chemical reduction of a palladium salt in an aqueous or organic solution with reducing agents such as hydrazine,[22] hydrogen[17,33] and sodium borohydride[34] has been described. We obtained the palladium(0)/magnesium-lanthanum mixed oxide by reduction of the palladium(II)/magnesium-lanthanum mixed oxide with hydrazine hydrate (Scheme 1).

The resulting samples were studied by ICP-OES in order to determine the amount of palladium dispersed the solid. The absolute metal content of the catalyst was 0.84 and 0.73 mmol/g in palladium(II) and in palladium(0) species, respectively.

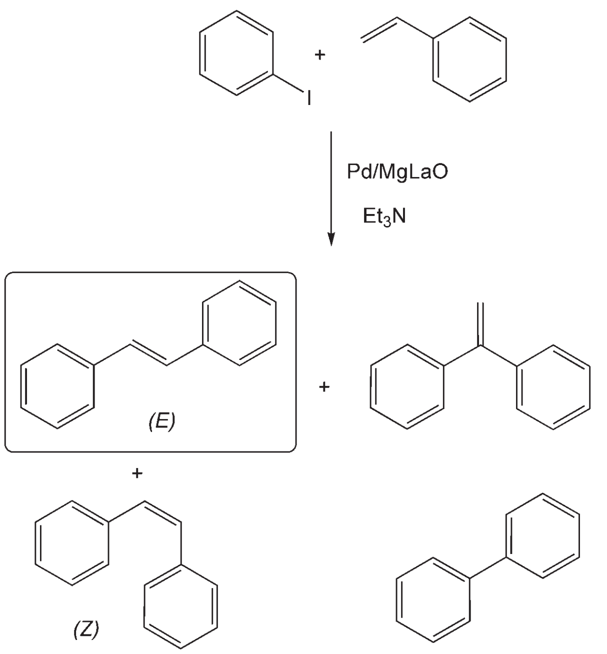
The Catalytic Activity of Palladium/Magnesium-Lanthanum Mixed Oxide

The activity of palladium immobilized on magnesium-lanthanum mixed oxide was examined in the Heck coupling reaction. Some reaction parameters (solvent, reaction time and base concentration) were investigated to determine the optimal conditions. Iodobenzene and styrene were chosen as model compounds for the initial study (Scheme 2). The reactions were performed with a 10% molar excess of styrene at 80 °C under ambient atmosphere in the presence of triethylamine.

When DMF was used as solvent, the coupling reaction provided an excellent yield after 10 h even when the



Scheme 1. Synthesis of the catalyst.



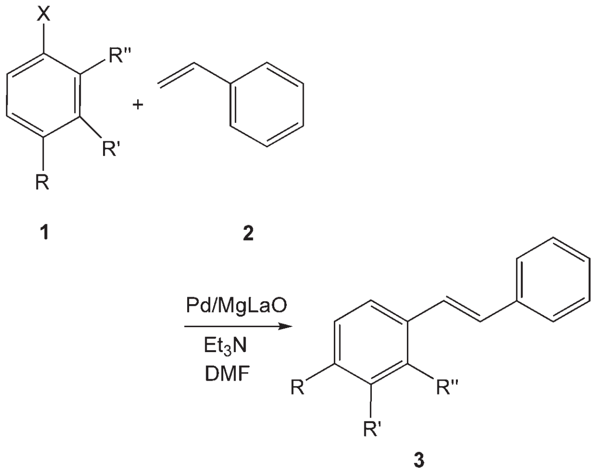
Scheme 2.

amount of the catalyst was reduced to 0.02 g (1.5 mol % of palladium) (Table 1, entry 4). Only the *trans*-arylation product was obtained selectively. Neither a biaryl derivative, resulting from a competing homocoupling reaction, nor branched derivatives were detected as by-products (Scheme 2). The solvent had a determinant effect on the yield of the product. On changing to the less polar toluene the yield decreased dramatically to 22% (Table 1, entry 5). In the reaction without triethylamine only a 5% yield of desired stilbene was obtained (Table 1, entry 6). This is in agreement with the currently accepted mechanism for the Heck reaction that requires the stoichiometric neutralization of hydrohalogenic acid by an appropriate base.

To compare palladium(II) with palladium(0), the reaction of iodobenzene and styrene was performed using 1.7 mol % of palladium(II)/magnesium-lanthanum mixed oxide in DMF in the presence of triethylamine as base. In this case only 44% yield was obtained (Table 1, entry 7) which is in agreement with the considerations described by Djakovitch and Koehler[17] that palladium(0) was the active species in heterogeneous systems.

Since aryl iodides are expensive substrates on a large scale, after the initial optimization studies with iodobenzene and styrene, we reacted a wide variety of aryl halides with styrene (Scheme 3) in the presence of the new catalyst system. In all cases *E* isomers were obtained exclusively. The conversion in the reactions depended on the nature of the halides and their substituents.

The best result was obtained in the reaction with the highly reactive iodobenzene. With bromobenzene a slower reaction was observed, but increasing the reaction time from 10 h to 20 h led to higher reaction yield (Table 2, entry 3). With chlorobenzene the coupling reaction afforded only 17% yield even after a longer reaction time (25 h), at a much lower temperature than usually used for activating aryl chlorides. The yields de-



Scheme 3.

Table 1. Effect of the solvent and the amount of catalyst on the yield.[a]

Entry	Solvent	Reaction time [h]	Catalyst [g] (mol % Pd)	Yield [%][b]
1	DMF	20	0.1 (7.3)	99
2	DMF	10	0.1 (7.3)	95
3	DMF	10	0.05 (3.7)	95
4	DMF	10	0.02 (1.5)	95
5	Toluene	10	0.05 (3.7)	22
6	DMF	10	0.02 (1.5)	5[c]
7	DMF	10	0.02 (1.7)	44[d]

[a] *Reaction conditions:* 1 mmol aryl halide, 1.2 mmol olefin, 1.2 mmol triethylamine, 80 °C.
[b] Yield of isolated product.
[c] Without triethylamine.
[d] Palladium(II)/magnesium-lanthanum mixed oxide catalyst.

Table 2. Heck reaction between aryl halides and styrene in the presence of palladium/magnesium-lanthanum mixed oxide catalyst.[a]

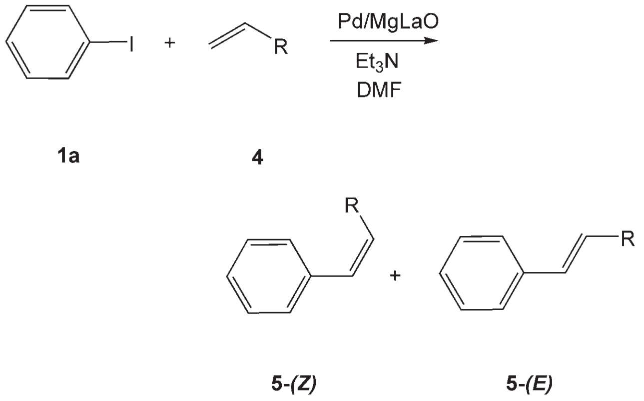
Entry	Product	X	R	R′	R″	Reaction time [h]	Yield [%][b]
1	**3a**	I	H	H	H	10	95
2	**3b**	Br	H	H	H	10	11
3	**3b**	Br	H	H	H	20	67
4	**3c**	Br	$COCH_3$	H	H	20	90
5	**3d**	Br	H	H	$COCH_3$	20	95
6	**3e**	Br	CH_3	H	H	20	73
7	**3f**	Br	H	CH_3	OH	20	66
8	**3g**	Cl	H	H	H	25	17
9	**3h**	Cl	$COCH_3$	H	H	20	72
10	**3i**	Cl	H	H	$COCH_3$	20	70
11	**3j**	Cl	CHO	H	H	20	80
12	**3k**	Cl	H	H	CHO	20	78

[a] *Reaction conditions:* 1 mmol aryl halide, 1.2 mmol styrene, 1.2 mmol triethylamine, 1.5 mol % palladium, 5 mL DMF, 80 °C.
[b] Yield of isolated product.

creased in the expected order I > Br > Cl. As expected, better results were obtained in the presence of activated aryl bromides and chlorides such as 4-bromoacetophenone, 4-chlorocetophenone, or 4-chlorobenzaldehyde (Table 2, entries 4, 9, and 11). When a bromobenzene derivative with an electron-donating substituent was used as reactant (*p*-bromotoluene), the yield of the product decreased. Interestingly, the sterically hindered 3-methyl-2-bromophenol (entry 7) could also be coupled with styrene in 66% yield under the above-mentioned reaction conditions. There was no example found in the literature where aryl chlorides would react at such a low temperature with good yield.

The steric effects of the acetyl group in the *ortho* position (2-bromoacetophenone, 2-chloroacetophenone and 2-chlorobenzaldehyde; Table 2, entries 5, 10 and 12) did not influence the yield significantly. These results suggest that the electronic factors are determining for the rate of this reaction with palladium/magnesium-lanthanum mixed oxide.

Next, we examined the efficiency of the palladium/magnesium-lanthanum catalyst in the arylation of other unsaturated compounds, acrylates, butyl vinyl ether and 1-hexene. In spite of the stereoselectivity observed in the reaction between iodobenzene and styrene leading to the exclusive formation of the *E* isomer, in these experiments in some cases mixtures of the linear isomers *E* and *Z* were obtained (Scheme 4, entries 2, 3). The branched product was not observed in these cases either.



Scheme 4.

All the reactions were performed in the presence of palladium/magnesium-lanthanum catalyst with 1.2 mol equivs. of triethylamine in DMF at 80 °C for 10 h. In all cases the corresponding coupling products were obtained in good to excellent yields (Table 3). The *E*/*Z*

Table 3. Palladium/magnesium-lanthanum mixed oxide-catalyzed Heck reaction with iodobenzene.[a]

Entry	Product	R	Reaction time [h]	Yield [%]	*E*:*Z*[b] ratio
1	**5a**	COOEt	10	75	100:0
2	**5b**	CN	10	80	81:19
3	**5c**	OBu	10	96	50:50
4	**5d**	*n*-Bu	10	75[c]	100:0
5	**5e**	$C(CH_3)_2OH$	10	80	100:0

[a] *Reaction conditions:* 1 mmol iodobenzene, 1.2 mmol alkene, 1,2 mmol triethylamine, 1.5 mol % palladium, 5 mL DMF, 80 °C.
[b] Calculated by ^1H NMR.
[c] Reaction temperature: 60 °C.

stereoselectivity was determined from the coupling constants of the products in the ^{1}H NMR spectra.

An important conclusion of this work is the much higher activity of the palladium/magnesium-lanthanum mixed oxide compared to palladium supported on acid supports such as carbon, zeolites, MCM-41-type materials or oxides. All these solids catalyze the reaction of bromobenzene and styrene at 140 °C for palladium on charcoal or on zeolites, 160 °C for palladium on oxides,[35] and 170 °C for palladium on MCM[36,37] or on SBA.[38] By contrast, hydrotalcite modified by exchange onto the surface of triphenylphosphine sulfonate works at 120 °C.

The mechanism of the reaction is supposed to involve as first step the oxidative addition of the halocarbon on a zerovalent palladium atom.[2,3] This step is the one also involved in the hydrogenolysis of C–Cl bonds, therefore it is not surprising that a strong effect of the support is observed in both cases. Both reactions should be affected indirectly by the support through the change of the availability of electrons at the palladium surface.

Recycling of the Catalyst

The lifetime is an important point concerning the use of the catalyst both for industrial and pharmaceutical applications. As the solid catalyst can be recovered easily from the reaction mixture, we examined the reuse of the catalyst in the reaction of iodobenzene and styrene. After the first run the catalyst was separated by filtration, washed with hexane to remove adsorbed organic substrates and then allowed to dry at room temperature.

The recycled palladium/magnesium-lanthanum mixed oxide was then reused in the presence of triethylamine in DMF without any regeneration at 80 °C. Figure 1 presents the results of recycling of the catalytic system. It was found that four catalyst runs were performed without any significant loss of catalytic activity (the use of 0.02 g of catalyst gave 95%, 95%, 93%, 90% isolated yield of *E*-stilbene for the 1st, 2nd, 3rd, 4th cycles, respectively). The catalyst was not sensitive to the humidity in the air, it could be stored under air without any loss of activity.

The decrease of activity suggests some small deactivation or leaching of palladium. It is still disputed whether the reaction takes place on the solid palladium surface[14,39] or with palladium dissolved from the catalyst.[40–42] The test used to discriminate between the two possibilities is to make a "hot filtration" and run the reaction with the metal remaining in the solution. If palladium has been leached the reaction could proceed by homogeneous catalysis. Hot filtration is required to exclude the possibility of precipitating the dissolved palladium onto a support during cooling to room temperature, so that the catalyst could maintain its catalytic activity. This behavior has been observed, e.g., in the palladium on charcoal catalytic systems and has been described as the "boomerang effect".[43,44] Indeed Alonso et al.[45] have reported that palladium contents as low as 10^{-8} mol % catalyze the Heck reaction of bromobenzene on methylacrylate at 160 °C, so that it is difficult to exclude the catalysis by leached palladium species. It has to be emphasized, however, that in this case the reaction was run a temperature higher by 100 °C than that used here. The palladium content of the filtered solid was determined by ICP-OES. The difference between the fresh and used catalyst was *ca.* 4%. If we assume that this mass is exclusively leached palladium, this would correspond to 6×10^{-3} mol % palladium in solution.

The reaction of iodobenzene on styrene was used as model: iodoaryl derivatives are very reactive and it is then expected that if palladium was leached, the reaction could proceed in solution. The reaction mixture was stirred for 2 h, then the solid catalyst was filtered off at the reaction temperature. The 46% conversion at this point was determined by ^{1}H NMR spectroscopy from a sample taken from the filtrate. Then the supernatant was allowed to react further in the absence of the solid catalyst under identical reaction conditions. Figure 2 shows that, after removal of the solid, the reaction stopped. If the reaction does proceed with trace amounts of palladium in solution, these traces are trap-

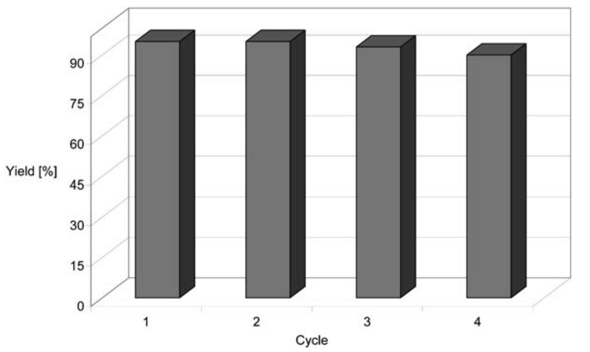


Figure 1. Yields obtained with recycled catalyst.

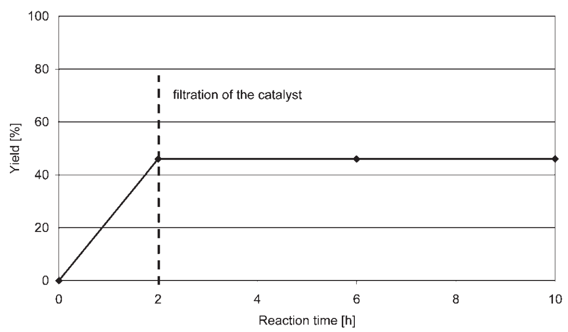


Figure 2. Evolution of the yield as a function before and after catalyst filtration.

ped by the solid in the filtration. However, the observation of a strong support effect on the activity of palladium suggests that the reaction occurs at the surface.

Conclusion

In summary, we have developed a new heterogeneous palladium/magnesium-lanthanum mixed oxide catalyst, which catalyzed efficiently the coupling reaction of aryl halides with a variety of olefins. The conversion in the reactions depends on the nature of the aryl halide. The reaction is regioselective and stereospecific. The reactions can be performed with 1.5 mol % palladium at 80 °C. The catalyst can be recovered by simple filtration and reused without significant loss of activity under ambient atmosphere. The catalyst is air stable, can be stored and handled also under an atmosphere of air.

Experimental Section

Commercially available starting materials were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer using TMS as internal standard. Melting points were determined on Gallenkamp apparatus and are uncorrected. TLC was performed on Merk Kieselgel plates (60 F_{254}) with hexane:acetone (4:1) as eluent. The surface areas were determined from the isotherms of adsorption of N_2 at 77 K using the BET equation. X-ray powder diffraction (XRD) patterns were recorded on a Philips instrument using CuKα_1 radiation ($\lambda = 1.54184$ Å). The palladium content was determined by ICP-OES. The spectral and physical data of the known compounds were identical with those reported in the literature.

Preparation of Magnesium-Lanthanum Mixed Oxide

Magnesium and lanthanum nitrates (0.386 mol and 0.129 mol in 0.5 L water for an atomic ratio Mg/La = 3) were coprecipitated at a constant pH = 10 using a mixture of potassium hydroxide (1 mol) and potassium carbonate (0.26 mol) in 0.52 L of distilled water. The samples (about 0.15 g) were activated at 923 K. The chemical analyses of the solid catalyst gave the composition: La: 39.8%, K: 5.4%, H_2O: 37%. The Mg/La ratio in the solid is then 4.26, compared to 3 in the solution, therefore the precipitation of lanthanum is not complete at pH 10. The powder XRD pattern of the uncalcined magnesium-lanthanum mixed oxide contains diffraction lines of a hydrated lanthanum carbonate as well as magnesium and lanthanum hydroxides. This triphasic solid probably consists of a layer of lanthanum oxide deposited on magnesia. The surface area of this mixed oxide is 37.6 m^2/g after calcination at 923 K, and supporting lanthanum on magnesia thus renders the surface area stable. The enthalpy of adsorption of CO_2 as measured by microcalorimetry allows us to evaluate the basic strength of the solid, and the number of basic sites is then measured by the amount adsorbed. Magnesium-lanthanum mixed oxide decarbonated at 673 K is a strong base, adsorbing about 10 mmol/g of CO_2 with an enthalpy >140 kJ/mol. This base strength is significantly higher than that of potassium fluoride supported on γ- or α-alumina, for which enthalpies of adsorption below 120 kJ/mol have been determined. Calcined, then hydrated hydrotalcite (HDT-OH) adsorbed about 0.25 mmol/g with a constant heat of adsorption of 100 kJ/mol, so magnesium-lanthanum mixed oxide appears to be a stronger base with a smaller number of sites.

Preparation of Palladium(II)/Magnesium-Lanthanum Mixed Oxide

Magnesium-lanthanum mixed oxide (1.5 g) was suspended in 150 mL of aqueous sodium tetrachloropalladate(II) (0.441 g, 1.5 mmol) solution and stirred at 25 °C for 12 h under a nitrogen atmosphere. The solid catalyst was filtered, washed thoroughly with 500 mL of water, and vacuum-dried to obtain the brown-colored palladium(II)/magnesium-lanthanum mixed oxide (0.84 mmol of Pd/g).

Preparation of Palladium(0)/Magnesium-Lanthanum Mixed Oxide

The catalyst (1 g) was reduced with hydrazine hydrate (1 g, 20 mmol) in ethanol (10 mL) for 3 h at room temperature, filtered, and washed with ethanol to give an air-stable black powder (0.73 mmol of Pd/g).

General Procedure for the Heck Reaction

In a typical reaction, palladium/magnesium-lanthanum mixed oxide catalyst (0.02 g, 1.5 mol % Pd) was added to a mixture of aryl halide (1 mmol), olefin (1.2 mmol), and triethylamine (1.2 mmol) in DMF (5 mL). The mixture was stirred at 80 °C for 10–25 h. Then the catalyst was filtered out, and washed with hexane. The reaction mixture was diluted with water and extracted with hexane (2 × 10 mL). The combined organic extracts were washed with water and brine, dried over magnesium sulfate and evaporated to give the product. The residue, if necessary, was purified by column chromatography or recrystallized to give the corresponding olefin. The known products were characterized by comparing the ^{1}H NMR, and melting point data with those reported in the literature.

Selected Data

(*E*)-Stilbene (**3a**): white solid, mp 122–123 °C (methanol) (lit. 123–124 °C[47]); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.11$ (s, 2H), 7.23–7.28 (m, 2H), 7.33–7.38 (m, 4H), 7.48–7.50 (m, 4H); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 137.4$, 128.5, 127.5, 126.6.

(*E*)-Cinnamonitrile and (*Z*)-cinnamonitrile were isolated as an *E*:*Z* mixture (**5b**). (*E*)-**5b**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.87$ (d, 1H, $J = 16.6$ Hz), 7.39 (d, 1H, $J = 16.6$ Hz), 7.38–7.50 (m, 5H). (*Z*)-**5b**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.44$ (d, 1H, $J = 12.3$ Hz), 7.13 (d, 1H, $J = 12.3$ Hz), 7.38–7.50 (m, 5H).

Recycling of the Palladium/Magnesium-Lanthanum Mixed Oxide Catalyst

Reactions were carried out as described above in the General Procedure using iodobenzene and styrene as reactants. After filtration of the alkene products, the solid palladium/magnesium-lanthanum mixed oxide catalyst was washed with hexane (5 mL) and dried at room temperature. Then the substrates were added and the coupling reaction was repeated as described.

Leaching Test

Leaching of palladium from the solid to the solution was studied in the reaction of iodobenzene and styrene, which was performed as described above. After 2 h the catalyst was filtered hot. Then the supernatant was allowed to react for additional 8 h, and then the samples of the reaction mixture were analyzed by ^{1}H NMR. In addition, the amount of palladium in the used catalyst was determined using ICP-OES as 0.7 mmol of Pd/g catalyst.

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