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Functional resins in palladium catalysis: promising materials for Heck reaction in aprotic polar solvents

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Abstract

The performances of palladium metal catalysts supported by organic resins containing tertiary amino, cyano, carboxyl, and pyridyl groups have been investigated in standard Heck reactions. The catalysts were prepared by either immobilization in the resins of palladium(II) precursors and chemical reduction thereof or by deposition of solvated metal atoms obtained by means of metal vapor synthesis (MVS). Particular attention was paid to the nature of catalysis in the presence of these materials. As the observed catalytic activity turned out to be generally associated with metal leaching, the reaction was most likely catalyzed in solution by soluble, active palladium species. However, a MVS 1% (w/w) catalyst supported by a commercial polyvinylpyridine resin cross-linked with divinylbenzene exhibited an appreciable catalytic activity with a possible partial contribution from supported active palladium species.

Keywords: Heck reaction; Palladium; Functional resins; Polyvinylpyridine; Metal vapor synthesis

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1. Introduction

Research on heterogenous palladium metal catalysts for the arylation of alkenes with aryl halides (Heck reaction) has recently gained considerable momentum. In 2001 we published a review [1] covering this field from its beginnings in the early 1970s up to that year, which contains about 40 strictly pertinent citations. An inspection of the literature reveals that the number of relevant papers published from 2001 to date is comparable, that is, the scientific production of the last four years on heterogeneous metal catalysis as applied to the Heck reaction has been almost the same as that of the preceding three decades. This is mainly due to the general recognition of heterogeneous catalysis as a valuable tool in the synthesis of fine chemicals [2]. Homogeneous catalytic systems for the Heck reaction are usually based on a palladium salt or complex and, usually, an additional ligand [3]. The workup of the reaction mixtures is often more complicated than desirable for industrial practice. Therefore, although the Heck reaction is unquestionably one of the most promising metal-catalyzed synthetic routes to fine chemicals, the number of its technical applications is not as large as could be expected [3b], in spite of recent considerable progress in this direction [3c].

Recent research on heterogeneous catalysts for the Heck reaction is mainly focused on solid-supported palladium systems, which are amenable to easy separation of the catalyst from the reaction mixture. These catalysts can be based on either supported palladium metal (i.e., “classical” heterogeneous catalysts) or supported palladium complexes. Catalysts of the latter type are not heterogeneous in the classical

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sense, in that the active sites do not belong to the metal surface, but are molecularly defined palladium centers chemically bound to a solid support ("hybrid" catalysts) [4]. In any case, the support must be able to completely retain the metal (palladium) at the end of the reaction to achieve efficient separation. This is very difficult to obtain with hybrid catalysts, since even seemingly very robust supported palladium complexes have been found to decompose under Heck reaction conditions, releasing active palladium species in solution [5]. In this respect, a catalyst containing supported palladium nanoparticles could be expected to be more efficient than a hybrid one. However, in polar aprotic solvents, like N,N-dialkylamides, palladium is generally also leached out from (would-be) classical heterogeneous catalysts, and the apparent activity in the coupling reaction stems from soluble species released into the bulk liquid phase [1,6]. Several recent pieces of information from the work of Kohler [7] and Arai [8] confirmed this circumstance, but also showed that under proper conditions the support effectively scavenged the metal from the solution after reaction, so that its practically quantitative recovery as supported metal nanoparticles was possible. In spite of this, as highlighted by Kohler and co-workers, recycling of the recovered catalyst in batch reactions is not attractive, because of the dramatic restructuring of the metal nanoparticles [7a]. After being leached during the reaction, the metal re-precipitates on the support from the reaction mixture, yielding a material quite different from the fresh catalyst. Kohler and co-workers tried to achieve true heterogeneous catalysis on the surface of palladium nanoparticles by using sodium formate as both base and reductant. Under these conditions, metal leaching was largely (but not completely) prevented; however, the hydrodehalogenation of the aryl halide turned out to be the main reaction [7b]. Kohler attributed the formation of hydrodehalogenation products to a heterogeneous process taking place over large palladium nanoparticles, with the Heck coupling still promoted in solution by leached palladium [7b]. Kohler's results were substantially confirmed independently by Mukhopadhyay [9].

Unambiguous examples of a leaching-free hybrid Heck catalyst were reported by Jacobs and co-workers [10] and by Corma and co-workers [11]. They found that palladium salts supported on zeolites did not undergo metal leaching during Heck couplings in aromatic hydrocarbons. However, the activity observed in these solvents was too low for practical applications (it is well known that Heck reactions in aromatic hydrocarbons are much slower than in alkylamides), and unfortunately in N,N-dimethylacetamide the catalysts underwent metal leaching during the reaction. A more effective, apparently leaching-free hybrid catalyst made of palladium(II) centers grafted to the oxygen atoms of phosphate groups of hydroxyapatite was recently described by Kaneda [12].

Concerning classical heterogeneous metal catalysts, impressive results were obtained by Choudary and co-workers, who used a layered double hydroxide as the carrier of 4–6-nm palladium nanoparticles [13]; the resulting catalyst was even able to activate aryl chlorides. The key feature of this system is the use of an anhydrous molten tetraalkylammonium salt as the solvent instead of, for example, N-methylpyrrolidone. Choudary proposed that the reaction mechanism was similar to that of homogeneous catalysts. He collected evidence for the existence of [Pd(Ar)X] species in the recovered catalyst and argued that they were located on the surface of the metal nanoparticles, mainly on the basis of a low leaching level during the reaction and the absence of activity in the filtrate after the separation of the solid catalyst. He concluded that the catalyst was truly heterogeneous in the classic sense. However, Choudary's results suggest that truly heterogeneous activation (if any) of aryl halide and the olefin would bring aryl groups and hydrides close to one another over the metal surface. Under this circumstance it is rather surprising that no biaryls or hydrodehalogenation products were found (see above).

Further claims, not as impressive, of truly heterogeneous classical metal catalysts were recently reported by Mandal et al. [14], Molnar et al. [15], and Shimizu et al. [16], who used palladium particles dispersed on inorganic supports previously functionalized with different groups (primary amino groups, Si–H and SH functions).

In conclusion, the number of heterogeneous Heck catalysts that are unambiguously leaching-free is still very limited; moreover, examples of leaching-free palladium metal catalysts are confined at present to the use of previously ad hoc functionalized inorganic supports and/or of peculiar reaction solvents such as molten tetralkylammonium salts.

In view of our previous experience with resin-supported metal palladium catalysts [17], also encompassing the Heck reaction [6a], we have investigated the possibility of exploiting functional cross-linked polymers as supports for palladium metal. Although polymeric supports have been relatively widely used to bind homogeneous Heck catalysts to an easily recoverable solid [5,18], organic resins used as supports for palladium metal catalysts have apparently been considered [19] much less in comparison with inorganic supports.

We herein report on our results for the Heck couplings of iodobenzene with methylacrylate and methylvinylether, chosen as standard reactions, in the presence of palladium catalysts supported on cross-linked (2–4% mol/mol) acrylic or vinylic resins bearing tertiary amino, cyano, carboxyl, and pyridyl functional groups.

2. Experimental

2.1. Materials and apparatus

All chemicals were from commercial sources and used as received, if not otherwise stated. The monomers (N,N-dimethylamino)ethylmethacrylate, cyanoethylacrylate, methacrylic acid) and cross-linkers (divinylbenzene, triethyleneglycoldimethacrylate) for the synthesis of the resins were obtained from Aldrich. Mesitylene, *n*-pentane, ethylvinylether, methylacrylate, iodobenzene, and *N*-methylpirrolidone were supplied by Fluka. Mesitylene and ethylvinylether were distilled over sodium before use. Triethylamine (from Aldrich) was distilled and stored over KOH pellets before use. Palladium acetate and sodium borohydride were obtained from Aldrich. CF4 was a commercial 2% divinylbenzene cross-linked polyvinylpyridine resin purchased from Aldrich. The resins were ground with an IKA A10 impact grinder. Transmission electron micrographs were taken with a Philips CM200 microscope. Samples were obtained by mechanical milling of the solid material and subsequent dispersion in ethanol with an ultrasonic bath for 0.5 h. One drop of the suspension was poured onto a carbon-coated copper grid and finally dried at room temperature. Ultrafine sections (30-nm slices) were obtained with a Leica Ultracut-R ultramicrotome after the material was embedded in Araldite CY212. The reaction mixtures of catalytic runs were analyzed with a Perkin–Elmer 8600 gas chromatograph equipped with a fused silica capillary column (30-m length; 0.547 mm i.d.; stationary phase DB-1, 1.5 µm; carrier He) and a FID detector. Atomic absorption spectrophotometry (AAS) analyses were generally carried out with a Perkin–Elmer 4100 ZL spectrophotometer, equipped with an electrothermally heated graphite furnace and a longitudinal Zeeman effect background corrector. The AAS analyses for the palladium content in the catalysts obtained through palladium immobilization/chemical reduction were carried out by Programma Ambiente srl (Padova, Italy) according to the EPA 3051 + EPA 6020/A methods.

2.2. *Resin synthesis*

For the synthesis of CF1, CF2, and CF3, respectively, 32.9 g of 2-(N,N-dimethylamino)ethylmethacrylate, 30.0 g of cyanoethylacrylate, and 30.9 g of methacrylic acid were used. Each liquid monomer was mixed with divinylbenzene (55% mol pure) (2.17 g, 2.45 g, 3.51 g for CF1, CF2, and CF3, respectively). For D2, 9.82 g of 2-(N,N-dimethylamino) ethylmethacrylate and 0.18 g of triethyleneglycoldimethacrylate were mixed together. The obtained solutions were poured into 15-ml Pyrex vials with screw caps and bubbled with N_2 for a few minutes to strip dioxygen. The vials were then exposed to γ-rays from a ^{60}Co source up to complete or almost complete disappearance of any liquid phase. The total dose required was ca. 10.5 KGy for CF1 and CF2 and ca. 32 KGy for CF3. After careful breaking of the vials, the resins were recovered as glassy rods, which were soaked in 200 ml of methanol in a closed vessel. After standing for a few days, the CF1 and CF3 rods spontaneously broke into relatively large granules. After the suspension was decanted, the two resins were washed with a further 200 ml of methanol in a single portion, treated with three portions of diethylether (100 ml each) and allowed to vacuum-dry at 70 °C to constant weight. CF2 did not break in methanol. The rods were recovered, air-dried for a few days, and finally cut into small pieces with scissors. The amounts of recovered resins were 32.0 g for CF1 (91%), 30.5 g for CF2 (94%), and 28.7 g for CF3 (92%).

The resins were then ground with an impact grinder and sieved to obtain powders with diameters ranging from 180 to 400 µm. After that, the resins were finally washed in a Soxhlet apparatus (three to four extraction cycles per hour) with acetonitrile (CF1, 8 h), tetrahydrofuran (CF2, 24 h), and acetone (CF3, 24 h), respectively. The powders were finally recovered and vacuum-dried at 50 °C up to constant weight.

2.3. *Swelling measurements*

An exactly weighed amount of the dry resin (typically 1.00 g), ground and sieved to the 180–400-µm-diameter range, was placed in a short graduated glass column with silica frit and carefully packed. The column was then filled from the top with enough of the desired swelling agent as to ensure full swelling of the solid. The column was then stoppered and the system was allowed to reach equilibrium (24–48 h). Occasionally, the column was opened and the suspension was manually stirred with a glass rod, to allow proper packing of the material. The difference between the volume of the swollen resin and that of the dry material, as read directly from the graduated scale of the column, gives the bulk expanded volume value (BEV). The specific absorbed volume was measured by a related procedure. In this case, an exactly weighed (typically 0.2 g) amount of resin was placed in a glass column. Again the desired swelling agent was poured from the top in such an amount as to ensure full swelling of the solid. After equilibration, the excess swelling agent was drained by centrifugation, and the mass of the swollen resin was quickly measured. The difference between the masses of swollen and dry resin is the mass of absorbed swelling agent, which is converted into a specific absorbed volume by multiplying it by the liquid density.

2.4. *Preparation of CR catalysts*

2.4.1. *Metallation of Pd/CF1 and Pd/D2*

A solution of palladium acetate (44 mg) in 20 ml of anhydrous tetrahydrofuran was added to the desired resin (2 g: overall Pd/resin = 1.04%, w/w). A further 20 ml of solvent was used to rinse the solution flask and was poured into the reaction vessel. The suspension was allowed to stand, with occasional manual stirring, for at least 24 h. For Pd/D2 the complete fading of the liquid phase indicated complete uptake of the metal, which was further confirmed by AAS analysis. The recovered metallated resins were washed with tetrahydrofuran and diethylether and finally vacuum-dried overnight at 50 °C.

2.4.2. *Metallation of Pd/CF2*

A solution of $[PdCl_2(NCPh)_2]$ (72 mg) in 20 ml of acetone was added to the resin (2 g: overall Pd/resin = 1.00%, w/w). A further 20 ml of solvent was used to rinse the solution flask and was poured into the reaction vessel. The suspension was allowed to stand, with occasional manual stirring, for at least 24 h. The recovered metallated resin was washed with acetone and diethylether and finally vacuum-dried overnight at 50 °C.

2.4.3. *Metallation of Pd/CF4*

One gram of the resin was suspended in 5 ml of MeCN and allowed to stand overnight in a three-necked round-bottomed flask equipped with a bubble condenser. After the suspension was heated to 60 °C, a warm solution (60 °C) of $[PdCl_2(NCMe)_2]$ (25 mg) in 6 ml of acetonitrile was added to the suspended resin. The reaction mixture was gently stirred for 2 h at 60 °C, and the solid was then recovered by filtration, washed with three portions (10 ml each) of warm acetonitrile (60 °C), and finally vacuum-dried overnight at 50 °C to constant weight.

2.4.4. *Metal reduction*

The metallated resin, weighed exactly, was suspended in ca. 5 ml of absolute ethanol per gram of solid and allowed to stand overnight. After that, a freshly prepared solution of $NaBH_4$ in absolute ethanol (per gram of resin: 0.16 g $NaBH_4$ in 15 ml of solvent; $Pd/NaBH_4 \geqslant 40$) was added to the suspension, and the reduction was allowed to proceed, with occasional manual stirring, until the evolution of H_2 ceased. The suspension was then centrifuged, the liquid phase was removed with a pipette, and 10 ml of fresh solvent was finally added. The catalyst was washed with mild stirring for 3 h. This treatment was repeated a further three times (the final washing was prolonged to ca. 18 h). Finnaly, the catalyst was vacuum-dried overnight at room temperature.

2.5. *Synthesis of the solvated palladium atoms*

In a typical experiment, Pd vapor generated at 10^{-2} Pa by resistive heating of 500 mg of the metal in an alumina-coated tungsten crucible was co-condensed at liquid nitrogen temperature with mesitylene (MES) (100 ml) in a glass reactor described elsewhere [20]. Then the reactor chamber was heated to the melting point of the solid matrix (−40 °C), and the resulting red-brown solution was siphoned and handled at low temperature (−30/−40 °C) with the Schlenk tube technique. The metal content of the solution was assessed by atomic absorption spectrophotometry (AAS): the metal-containing mesitylene solution (1 ml) was heated over a heating plate in a porcelain crucible, in the presence of *aqua regia* (2 ml), four times. The solid residue was dissolved in 0.5 M aqueous HCl, and the solution was analyzed by AAS. The palladium content of the solvated metal solution was 1.9 mg/ml.

Table 1
Palladium content (% w/w) of MVS catalysts

Resin	CF1	CF2	CF3	CF4	D2
% Pd	0.93	1.00	0.96	0.96[a]	0.89[b]

[a] 0.67% w/w Pd for the corresponding CR catalyst.

[b] 1.00% w/w Pd or the corresponding CR catalyst (measured before metal reduction).

2.6. *Preparation of the MVS catalysts*

The desired functional resin (generally 2 g) was suspended in MES (5 ml). The solution of solvated palladium atoms (10 ml) was added to the suspension, and the mixture was stirred for at least 24 h at room temperature. The solution was removed and the material was washed with deareated *n*-pentane (three portions, 10 ml each) and dried at room temperature under reduced pressure (ca. 1 Pa). The amount of deposited palladium was determined as the difference between the initially solvated palladium atoms (19 mg) and the residual amount of the metal in the liquid phase. The latter was measured by AAS of the filtrate, as described in the previous section, or was taken as zero when the liquid phase became colorless. The metal contents of the catalysts, as from AAS, are listed in Table 1.

2.7. *Catalytic runs*

Nine milliliters of *N*-methylpyrrolidone (NMP), 10–20 mmol of the alkene, 5 mmol of the aryl halide, 5 mmol of anhydrous triethylamine, and the required amount of catalyst (5 µmol of palladium, 0.1 mol% with respect to the aryl halide) were introduced, with inert gas flush, into a 25-ml round-bottomed, two-necked flask equipped with a stirring magnetic bar, a bubble condenser, and a silicon stopper. A sealed Carius tube was used as the reaction vessel for ethylvinylether couplings. The reaction mixture was magnetically stirred at the desired temperature for the required time. When needed, small samples of the reaction mixture were taken from the stoppered side neck. For GC analysis the samples were treated with either water or 0.5 M aqueous HCl. The organic products were then extracted with diethyl ether. The organic layer was washed with water up to neutrality (if needed), filtered on celite, and finally dried over dry sodium sulfate. The amount of leached palladium was assessed by means of AAS analysis on 1-ml samples and mineralized as described above after filtration on Teflon filters (0.2 µm).

2.8. *Washing tests*

An exactly weighed amount of catalyst (ca. 50 mg, corresponding to ca. 0.005 mmol Pd for 1.00% catalysts) was suspended in 9 ml of NMP, and 0.56 ml (5 mmol) of iodobenzene was added to the suspension. The mixture was then heated for the desired time (2–24 h) at 75 °C (or at 125 °C for MVS-Pd/CF4). The amount of leached palladium was checked by AAS as described above after filtration on Teflon filters (0.2 µm).

2.9. *Check for activity in the liquid phase*

The presence of active homogeneous species in the liquid phase was checked for after the separation of the solid catalyst, according to Sheldon's criterion [21], during both the catalytic runs and the washing tests. To this end, after the desired time of pretreatment with iodobenzene or the catalytic reaction, the solid was separated from the hot liquid by filtration on a Teflon filter (0.2 µm) under an inert atmosphere. The hot liquid was transferred into a second reaction vessel and kept at the desired reaction temperature (for the mixtures from the washing tests, the base and the alkene were also added before the reaction was re-started). Any progress in the reaction was monitored by GC analysis as described above.

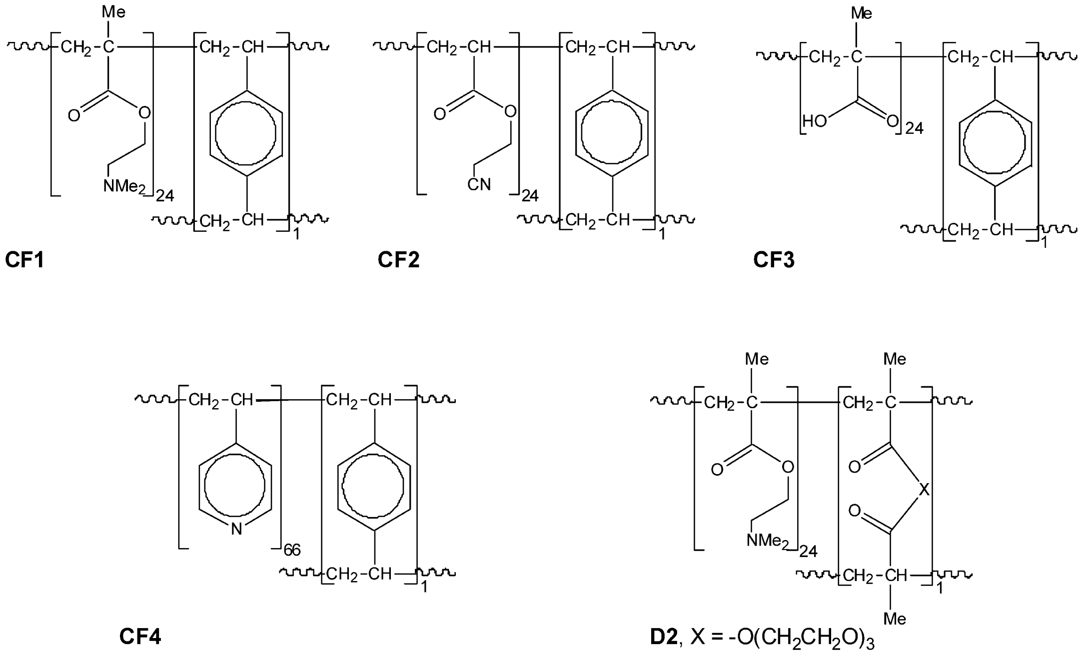
3. Results and discussion

The chemical structure of the resins used in the present study is sketched in Scheme 1.

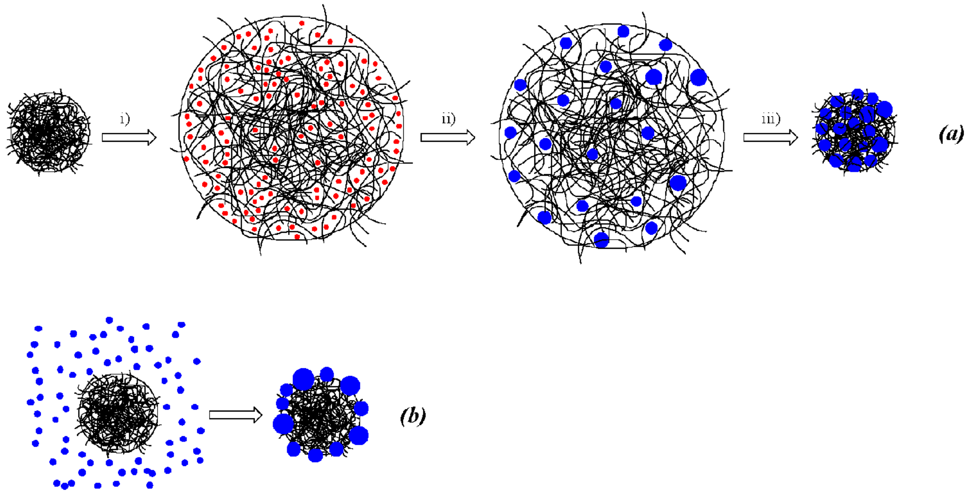
Resins CF1, D2, CF2, and CF3 were prepared by γ-ray polymerization (^{60}Co) of the parent monomers in the presence of divinylbenzene (cross-linker). CF4 is a commercial product.

Our organic resins are designed to exploit metal coordination: all of the functional groups used are in fact potential ligands (or precursors thereof) toward palladium(II). The resins were used to prepare supported palladium catalysts (1%, w/w Pd) with to two different procedures. In one case (chemical reduction route, CR), a palladium(II) complex was immobilized in the resin and subsequently chemically reduced with an alcoholic solution of $NaBH_4$ (Scheme 2a). In the other (metal vapor synthesis route, MVS) a complete set of catalysts was obtained by impregnation of the parent resin with mesitylene solutions of solvated metal atoms, prepared by co-deposition of solvent and metal vapors over a cold surface (metal vapor synthesis) [20] (Scheme 2b). The latter catalysts are hereafter referred to and coded as MVS. The distribution of palladium nanoparticles in the MVS catalysts was expected to be heterogeneous, with the metal concentrated on the outer surface of the support particles (see also below), since mesitylene is not a good swelling agent for the resins used.

Swelling can occur when a lightly cross-linked polymer is put in contact with a suitable liquid (swelling agent). The molecules of the swelling agent penetrate into the polymer framework and solvate the polymeric chains. As a result, the apparent volume of the resin increases and a microporous polymeric gel is formed. Broadly speaking, the higher the cross-linking degree of a resin, the lower its swelling ability (with the same chemical structure of the polymeric framework and the same swelling agent). When the degree of cross-linking is high enough, no appreciable swelling occurs. Microporosity in swollen resins is not permanent: upon removal of the swelling agent, the expanded polymer framework collapses back (shrinking). If the swelling agent is also a good solvent for some substance, the latter can diffuse into the swollen polymer, provided its molecules are small enough to enter the micropores. Thus, if the incorporation of the metal precursor and its subsequent reduction are accomplished by treatment with solutions of the required reagents in good swelling solvents, the spatial distribution of



Scheme 1. Sketch of the chemical structure of the resins employed as catalytic supports.



Scheme 2. Sketch of the CR (a) and MVS (b) routes to resin supported metal catalysts. (a): (i) resin swelling and immobilization of the metal precursor from the liquid phase, (ii) reduction to metal nanoclusters supported on swollen resin, (iii) resin drying and shrinking.

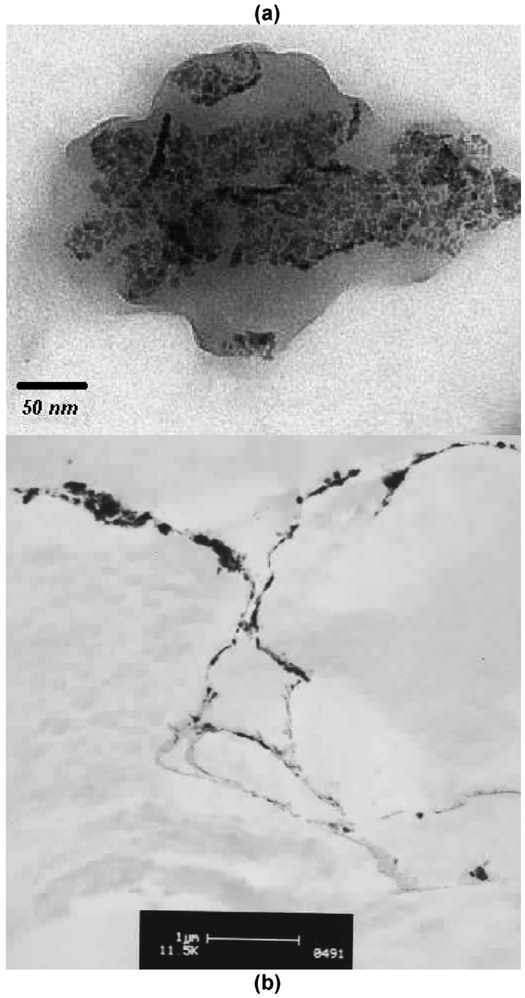
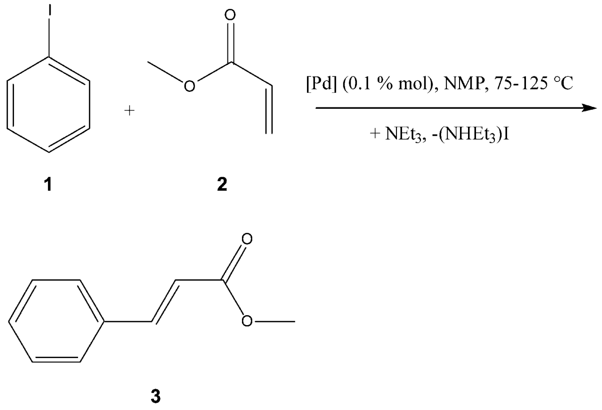


Fig. 1. TEM microphotograph of MVS-Pd/CF4: whole bead (a); ultrafine section (b).

the metal nanoclusters throughout the particle volume will generally tend to be homogeneous (Scheme 2a). On the other hand, if solvated metal atoms are deposited from a solution in a bad swelling agent, the metal supported nanoclusters in the final material will be formed on the outer particle surface (Scheme 2b). This was demonstrated for MVS-Pd/CF4 by TEM analysis (Fig. 1: (a) whole particle; (b) ultrathin section).

Although CF4 has a low cross-linking degree (2%), it is poorly swellable in most common solvents and particularly so in mesitylene (the swelling degree expressed as specific absorbed volume of mesitylene per gram of dry CF4 is as low as 0.2 cm^3/g) [22]. The deposition of palladium from a mesitylene solution of palladium solvated atoms yielded the expected peripheral distribution of the nanoclusters in the catalyst. Swelling generally has an adverse effect on the mechanical properties of lightly cross-linked resins. In general, the larger the swelling degree, the weaker the swollen material. This is one of the factors limiting the use of resins as catalytic supports.

The performance of the investigated catalysts was evaluated in the following reactions (with ethylvinylether, a higher temperature was generallyused because of the lower reactivity of the alkene):

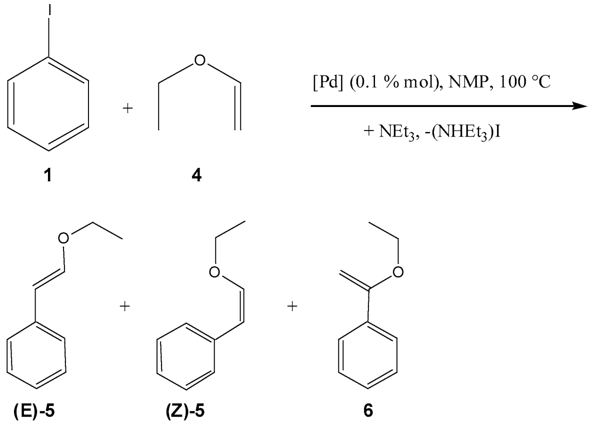


(1)

Table 2
Catalytic results in the coupling of iodobenzene with methylacrylate at 75 °C

Entry	Catalyst	Yield (%) (**3**)[a]	Time (h)	Remarks
1	$[Pd(OAc)_2]$	50	1	Homogeneous test
2	Pd/CF1	2	2	
		60	4	
3	MVS-Pd/CF1	50	1	
		88	2	
4	Pd/D2	2	2	
		68	4	
5	MVS-Pd/D2	39	1	
		79	2	
6	Pd/CF2	2	3	
		71	6	
7	MVS-Pd/CF2	20	4	
		51	6	
8	MVS-Pd/CF3	12	2	
		61	4	
9	MVS-Pd/CF4	4	2	
		60	48	
		67	4	$T = 100\,°C$
		96	2	$T = 125\,°C$
10	Pd/CF4	96	24	
		90	3	$T = 100\,°C$
		100	1	$T = 125\,°C$

[a] **3** (see Eq. (1)) was the only product detected.



(2)

Table 3
Catalytic results in the coupling of iodobenzene with ethylvinylether at 100 °C

Entry	Catalyst	Conversion (%)	Selectivity %			Time (h)
			(*E*)-**5**	(*Z*)-**5**	**6**	
1	$[Pd(OAc)_2]$[a]	55	20	27	53	4
		72	19	28	53	8
2	MVS-Pd/CF1	62	20	27	53	4
3	MVS-Pd/D2	68	20	29	51	4
		77	21	32	47	8
4	MVS-Pd/CF4	13	31	15	54	4
		26	15	20	65	8

[a] Homogeneous test.

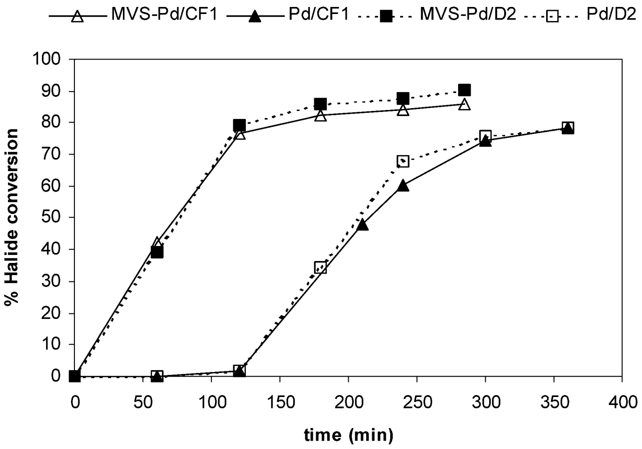


Fig. 2. Reaction progress in the coupling of iodobenzene with methylacrylate over CR and MVS catalysts supported on CF1 and D2.

When supported palladium metal is used as the catalyst for the Heck reaction, the activation step is likely represented by the attack of the metal by the aryl halide (see below). The interaction, if any, of basic groups (in the Lewis sense) with the metal surface could facilitate this process. In this connection, we have observed related catalyst promotion effects in the hydrogenation of cycloalkanes catalyzed by resin-supported palladium [17e].

The catalytic results are illustrated in Tables 2 and 3.

The reactions of methylacrylate are completely selective toward the E isomer of methylcinnamate. In the couplings of ethylvinylether both the β (**5**, E/Z mixture) and the α (**6**) regioisomers are formed. The observed regio- and stereoselectivities are comparable to those observed with homogeneous systems.

A comparison of the catalytic performances of Pd/CF1 and Pd/D2 (Table 2, entries 2 and 4) with those of MVS-Pd/CF1 and MVS-Pd/D2, respectively (Table 2, entries 3 and 5), shows that they are affected by the preparation method. In particular, the MVS catalysts exhibits much shorter (if any) activation times with respect to the non-MVS counterparts (Fig. 2). After the reaction onset, the rates are practically the same for all four catalysts, that is, activated CF1 and D2 catalysts are equally active, despite the preparation method. This suggests that the active form of the catalyst is the same for all of them and that the materials differ in the rate of its formation.

To highlight the real nature of the catalyst in these reactions, we monitored the palladium leaching into solution during the reaction for the most active of them (MVS-Pd/CF1). We found that the leaching started immediately and that 81% of the total palladium was present in solution after 1 h, corresponding to the maximum reaction rate (Fig. 3). As the reaction slowed the palladium concentration also subsided, and further stirring of the mixture for 8–12 h after cooling at room temperature lowered the amount of palladium in solution to 12–13% of total metal only.

These findings agree with the results of Kohler et al. [7], who showed a strict dependence of the reaction rate on the extent of leaching in Heck reactions catalyzed by palladium supported on carbon.

According to these results, the true catalyst is some soluble palladium species released into the liquid phase from

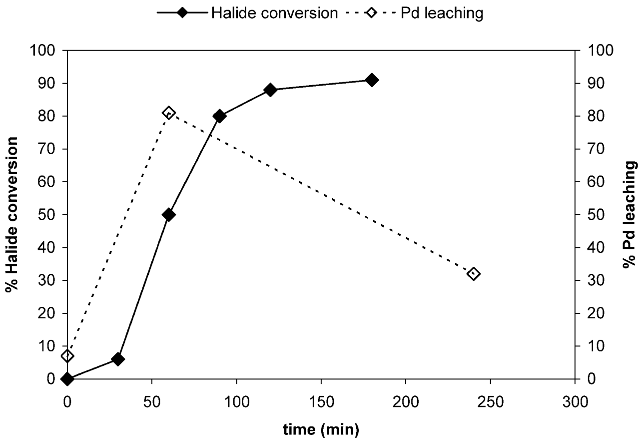


Fig. 3. Conversion (mol%) and palladium leaching (mol%) in the coupling of iodobenzene with methylacrylate over MVS-Pd/CF1.

Table 4
Metal leaching (percentage of total palladium) from MVS-Pd/CF1 and MVS-Pd/CF4 upon treatment with solutions of iodobenzene in NMP at 75 °C

Entry	Catalyst	Leaching degree (%)		
		2 h	4 h	24 h
1	Pd/CF1	–	5	–
2	MVS-Pd/CF1	45	–	50
			–	4[a]
3	MVS-Pd/CF4	0.09	–	0.08
		–	–	0.6[a]
		–	–	0.04[b]

[a] Only NMP.
[b] 125 °C.

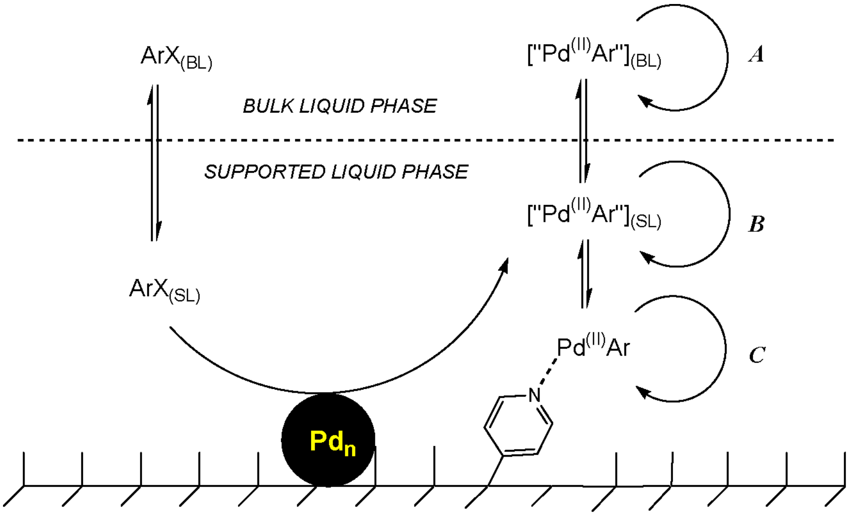
the solid. This is also in agreement with the results obtained by some of us with other resin-supported palladium catalysts [6a]. As the maximum reaction rate attained after “activation” is practically the same for all of the CF1 and D2 catalysts, the maximum degree of metal leaching is expected to be the same for all of them. Therefore, the difference between the MVS (relatively short activation time) and non-MVS (relatively long activation time) catalysts must be in the leaching rate.

Some of us have already found that palladium leaching is likely caused by the oxidative attack of the aryl halide on the metal nanoparticles, which yields haloaryl palladium(II) species in solution [1,6a]. During this investigation we obtained further support to this mechanism. When MVS-Pd/CF1 was washed with an iodobenzene solution in NMP, at the reaction temperature and for a prolonged time, 45% of palladium was leached in 2 h. This figure decreased to 4% when no halide was present (Table 4, entry 2).

The washing tests also confirmed the higher resistance to metal leaching of Pd/CF1 as compared with MVS-Pd/CF1 (Table 4, entries 1 and 2). With respect to real catalytic conditions, the leaching degree in the washing tests for MVS-Pd/CF1 at 75 °C was lower, probably because NEt_3 and the alkene, which are potential ligands for palladium(II), further helped its release into the liquid phase during the catalytic reaction. This is in agreement with our previous observation that the presence of good ligands in the liquid phase enhances the extent of metal leaching from supported palladium catalysts [6a]. Moreover, the leached species from washing experiments were very active in the liquid phase. After filtration of the hot mixture, to avoid the deactivation of any possible soluble active species, and the addition of methylacrylate and NEt_3 to the filtrate, the reaction went to completion in 4 h at 75 °C. If the solid was not filtered off after this treatment and methylacrylate and NEt_3 were added to the mixture, the conversion was quantitative in just 1 h; that is, the pretreatment of MVS-Pd/CF1 with the iodobenzene solution yielded a catalytic system much more active than the fresh catalyst. All of these findings support the hypothesis that the active species obtained from the attack of the aryl halide on the supported metal is a palladium(II) aryl derivative, which can directly enter the catalytic cycle and activate the alkene [1]. This is in line with the formation of palladium(II) aryl complexes observed by Reetz and Westermann in the stoichiometric reaction of PhI with stabilized palladium nanoclusters [23]. This leaves little doubt that the aryl halide is necessary for extensive leaching. Under these circumstances, the rate of palladium leaching from a resin-supported material could depend on several factors: (i) the rate of diffusion of the aryl halide from the bulk liquid phase into the support; (ii) the rate of oxidative attack of the halide on the nanoparticles; (iii) the spatial distribution of the metal nanoparticles within the support beads; (iv) the extent of formation of polymer-grafted palladium complexes; and (v) the rate of diffusion thereof from the support to the bulk liquid phase (Scheme 3).

When different catalysts based on the same support are compared, just like for Pd/CF1 and MVS-Pd/CF1 or Pd/D2 and MVS-Pd/D2, factors (i), (iv), and (v) can be neglected. The leaching rate differences will therefore depend on the nanoparticle size, which determines their reactivity toward the aryl halide, and on their spatial distribution (homogeneous or eggshell).

The metal nanoparticle sizes in Pd/CF1 and MVS-Pd/CF1 were assessed by means of TEM analysis (Fig. 4). The micrographs clearly show that the palladium nanoparticles are much smaller in MVS-Pd/CF1 than in Pd/CF1. In addition, the former catalyst was prepared by deposition of solvated palladium atoms from a mesitylene solution. CF1 does not swell to any extent in hydrocarbon solvents, and therefore palladium nanoparticles are expected to lie on the outer surface of the resin beads. In contrast, Pd/CF1 was obtained by reduction of palladium(II) species previously anchored to swollen CF1. The solvents used for the immobilization of the palladium precursor and its reduction were tetrahydrofuran and ethanol, respectively. The bulk expanded volumes (difference between the volume of swollen and dry resin, per gram of dry material) of CF1 in THF and ethanol were 1.0 and 1.7 cm^3/g, respectively. In view of this moderate swelling of CF1, a relatively homogeneous distribution of the metal nanoparticles through-



Scheme 3. Possible reaction pattern for a resin supported palladium catalyst in the Heck reaction. (A) and (B) catalytic cycles in the bulk (homogeneous catalysis of leached palladium species) and supported liquid phase (catalysis by soluble species within the catalyst particle); (C) catalytic cycle sustained by grafted palladium species (hybrid catalysis).

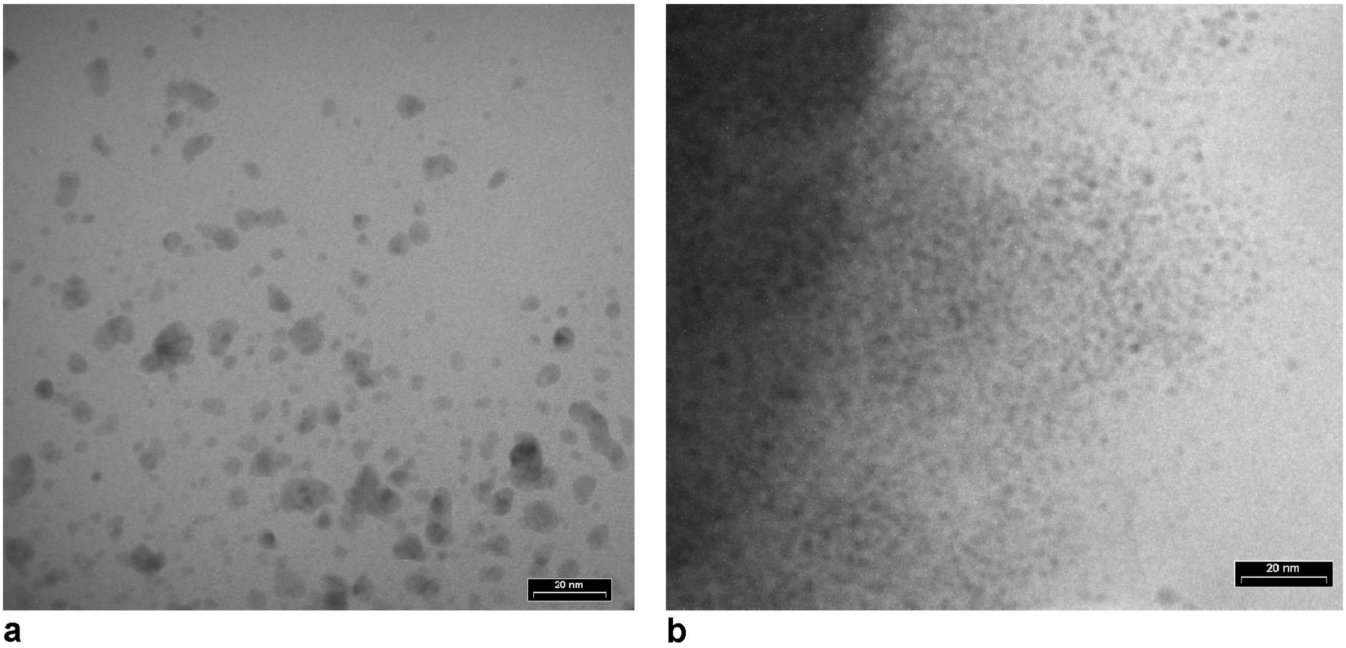


Fig. 4. TEM micrographs of Pd/CF1 (a) and MVS-Pd/CF1 (b).

out the resin beads was expected [17]. This accounts for the much higher rate of metal leaching in the MVS catalyst, where (comparatively) small palladium nanoparticles are located on (or close to) the surface of the catalyst beads.

On the basis of Scheme 3, it is clear that diffusion of the aryl halide toward the metal nanoclusters will be easier and that the oxidative attack of the halide on the metal nanocluster will be faster in a MVS-Pd/CF1 than in Pd/CF1. This process is supposed to yield a $[Pd^{II}(Ar)X]$ species, which starts the catalytic cycle [1] and whose diffusion into the liquid phase will be also easier in MVS-Pd/CF1 than in Pd/CF1. Our data, therefore, agree with the hypothesis that a $[Pd^{II}(Ar)X]$, or a related one, is the active species, formed during the leaching process, which builds up faster in solution in the case of MVS catalysts. Such a species is also supposed to take part in the catalytic cycle in the homogeneous, ligand-less Heck reaction [25a]. After metal leaching, the catalytic process in solution will likely be the same as in the homogeneous, ligand-less Heck reaction [1]. The nature of the active species in the latter process is still under debate, particularly as far as the direct involvement of palladium nanoclusters in the catalytic cycle is concerned [3c]. Therefore we did not investigate the nature of the palladium species in solution, as this was far beyond the scope of this paper.

MVS catalysts were prepared also with the supports CF2, CF3, and CF4. The apparent activity in the MVS set decreased in the following order: CF1 > CF3 > CF2 ≫ CF4 (Table 1, entries 3, 7–9). The time dependence of the conversion over the four MVS catalysts is presented in Fig. 5.

All of the catalysts but MVS-Pd/CF1 exhibited appreciable induction times. MVS-Pd/CF4 in particular was poorly active at 75 °C (Table 1, entry 9). The very low activity at 75 °C was associated with a very low extent of palladium leaching, ranging between 1.3 and 1.9% of total palladium (1.6% on average) during the reaction (Fig. 6).

This circumstance suggests that the different performances of the MVS catalysts at 75 °C were connected to different levels of palladium leaching during the reaction; that is, the amount of leached palladium decreased in the same order as the activity: CF1 > CF3 > CF2 ≫ CF4. In a comparison of different catalysts based on different supports, all of the factors (i)–(v) mentioned above should be taken into account. Some of them (the diffusion rates and the ability of the support to retain the palladium complexes) are very difficult to estimate, and therefore we cannot fully account for this sequence.

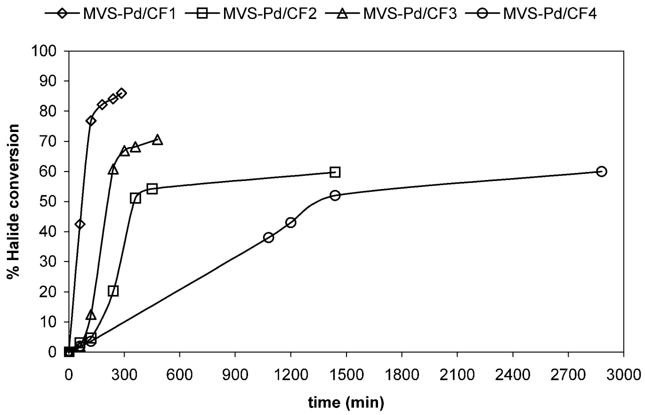


Fig. 5. Catalytic performance of 1% MVS resin-supported palladium catalysts in the coupling of iodobenzene with methylacrylate.

The case of MVS-Pd/CF4, supported by poly-{vinylpyridine} cross-linked with divinylbenzene (PVPy) (coded as CF4 in this paper), is a particularly interesting and intriguing one. In 1997 Antonietti reported that PVPy fully quenches the catalytic activity of homogeneous $[Pd(OAc)_2]$ (Pyridyl/Pd $= 7 \times 10^2$) [24]. He also found that molecular pyridine, in even larger excess, did not suppress the catalytic activity of the system and so concluded that PVPy is an effective scavenger of soluble palladium species from Heck reaction mixtures. These findings were confirmed later by Yu et al. in a quite recent investigation of SCS-pincer palladium complexes, both homogeneous and grafted to solid supports [5a]. These authors attributed this particular ability of PVPy to its insolubility and its excellent ability of binding to palladium. They also suggested that PVPy could also be a potential scavenger for soluble Pd(0) nanoclusters [5a]. On this basis, PVPy could be a very interesting catalytic support in Heck chemistry for obtaining leaching-free catalysts or a useful material for palladium recovery and recycling, in a way similar to that proposed recently by De Vries [25b]. In addition, we mentioned above that in general CF4 swells poorly in organic solvents [22]. Ensuing good mechanical stability should also help in limiting metal leaching, but at this stage we decided not to address this question. However, further work aimed at lowering the extent of palladium leaching, if possible, will also need to take into account this parameter.

As shown above and later on, the extent of palladium leaching for MVS-Pd/CF4 was low during the reaction, at both 75 and 125 °C. In spite of this, the activity of this catalyst (Fig. 6 and Table 2, entry 9) at 100 and 125 °C is comparable to that of other supported systems (see Ref. [5a] for a recent example). Remarkably, the increase in temperature did not dramatically affect the extent of palladium leaching, as confirmed by both washing tests (Table 4) and by monitoring of the palladium concentration in solution during the

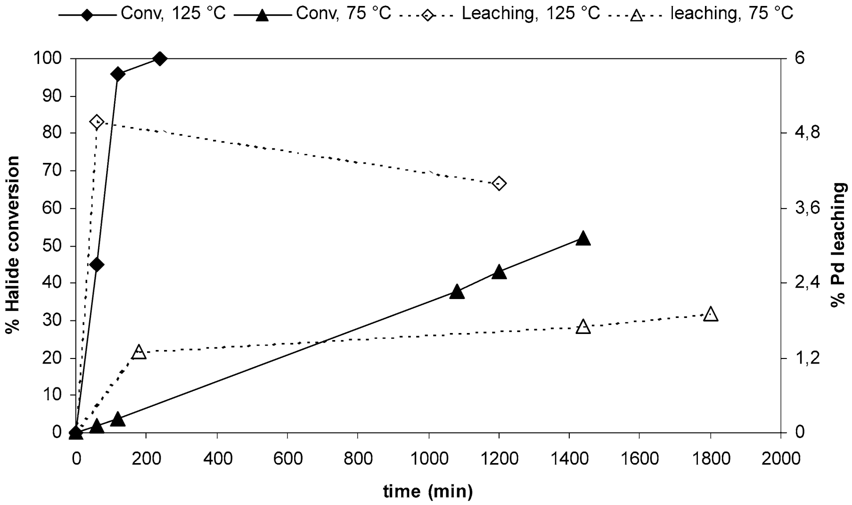


Fig. 6. Catalytic performance and palladium leaching in the coupling of iodobenzene with methylacrylate over MVS-Pd/CF4 at 75 and 125 °C.

reaction. Also in the case of CF4 we found that real reaction conditions allowed a much higher leaching level in comparison with washing tests. At 125 °C the amount of palladium leached during the reaction ranged between 4.2 and 5.2% of the total available metal, compared with the 1.3–1.9% range at 75 °C. The most straightforward explanation of the appreciable increase in activity with temperature is homogeneous catalysis sustained by the tiny amounts of palladium released into the bulk liquid phase. With only 4–5% of palladium leached out from the solid catalyst, the actual Pd/PhI molar ratio in solution, under the conditions used, would be 4–5 × 10^{-5}. Up to the first hour (i.e., up to 96% conversion) the reaction proceeded at a roughly constant rate. The TOF referred to the amount of leached palladium was about 10^4 h^{-1}, compatible with "homeopathic" ligand-less catalysis in solution [25a]. The catalyst was recycled at 125 °C, and the reaction was complete after 2 h, even in the second run. With these results in our hands, we tried to ascertain the nature of the catalytic action. In the first place, we found that the reaction stopped upon separation (according to Sheldon's recommendations [21]; see Section 2) of the catalyst after 1 h from the beginning of the reaction at 100 °C (conversion ca. 8%) (these tests are referred to hereafter as hot filtration tests, HFTs). The solid from the HFT was recycled in a subsequent catalytic run at 100 °C, where an 87% yield was achieved after 4.5 h, indicating that the performance of the recovered catalyst was the same as that of the fresh material (Table 3, entry 9), if not slightly better. This finding at first suggested that the leached palladium species were not involved in the catalytic process. This conclusion seemed to be reinforced by the fact that HFT showed the presence of active species in other cases investigated in this work. For instance, in the case of Pd/CF4, the non-MVS analog of MVS-Pd/CF4, the HFT at 100 °C showed an appreciable catalytic activity in solution after its separation from the reaction mixture (Fig. 7). This finding indicated that the leaching extent was higher for Pd/CF4 than for MVS-Pd/CF4 and that homogeneous catalysis in the bulk liquid phase contributed to the overall catalytic activity of the former.

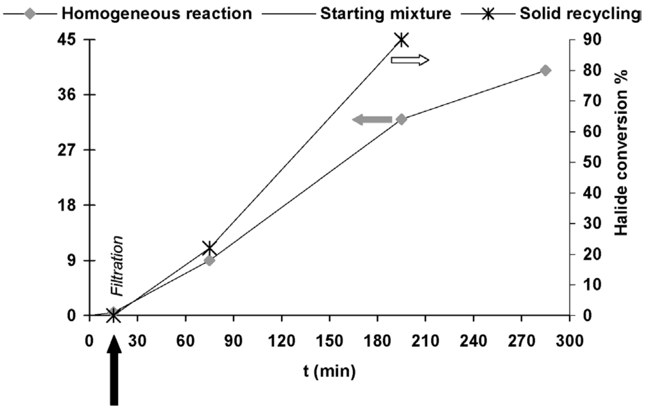


Fig. 7. Hot filtration test results for the coupling of iodobenzene with methylacrylate at 100 °C over Pd/CF4.

However, this was actually a single test demonstration, which is not enough to prove the heterogeneous nature of a supported catalyst under solid–liquid conditions, as pointed out by Widegren and Finke [26]. Moreover, with such a low leaching extent as that exhibited by MVS-Pd/CF4, a false negative response of the HFT could not be ruled out (see Ref. [27] for an example). Finally, the selectivity of MVS-Pd/CF4 was similar to those of both homogeneous catalysts and supported systems working on a palladium release basis.

We decided then to prepare a second stock of MVS-Pd/CF4, which turned out to be somewhat more active than the first one (90% yield after 3 h at 100 °C). We checked its performance at 100 °C (the same temperature of the HFT) in the presence of extra PVPy, with a large molar excess of pyridyl functions with respect to palladium. Yu et al. found that the addition of PVPy (Py/Pd = 150 mol/mol) to the reaction mixture in the Heck coupling of iodobenzene with n-butylacrylate at 120 °C quenched the catalytic activity of silica- or polystyrene-grafted SCS-pincer palladium complexes [5a], which were found to be positive to the HFT. On this basis they concluded that the catalytic action was homogeneous in nature and that these materials were only actually reservoirs of soluble, active palladium species.

In the case of MVS-Pd/CF4, the addition of an extra amount of PVPy (Py/Pd = 150; overall Py/Pd = 250, support + extra PVPy) has different effects, depending on the time of introduction into the reaction mixture. When PVPy was added 45 min after the beginning of the reaction at 100 °C (23% yield), the reaction did not stop (Fig. 8). The catalytic performance after 90 min (45 min after the addition of extra PVPy) was practically unchanged, and only toward the end of the reaction (yield > 70%) did we observe a slight decrease in the reaction rate. In contrast, the introduction of extra PVPy after the beginning of the reaction led to a reasonable decrease in the catalytic activity (Fig. 8). The induction time was longer than in the other two cases, and the slope of the central part of the sigmoidal reaction profile (which can be approximated by a straight line in all cases) was lower. In spite of this, the system was still appreciably active. From these plots we can roughly estimate that after the onset the apparent rate for the slowest reaction (extra PVPy after the beginning) was slightly less than the half with respect to the fastest one (MVS-Pd/CF4 alone).

These data prove that MVS-Pd/CF4 is not a fully leaching-free catalyst. They also show that the scavenging ability of extra PVPy is a function of the time of addition. This circumstance is likely due to changes with time in the nature of the palladium species in solution: apparently they stick to PVPy much more readily as soon as they are released. This should be taken into account for experiments with intentional metal scavenging, like those described by Yu et al. and in this paper.

If we consider that (i) we worked with a PhI/Pd molar ratio of 10^3 instead of 3.5 × 10^2, as used by Yu et al., and (ii) that MVS-Pd/CF4 was negative to the HFT, whereas the catalysts investigated by Yu et al. were not, we can specu-

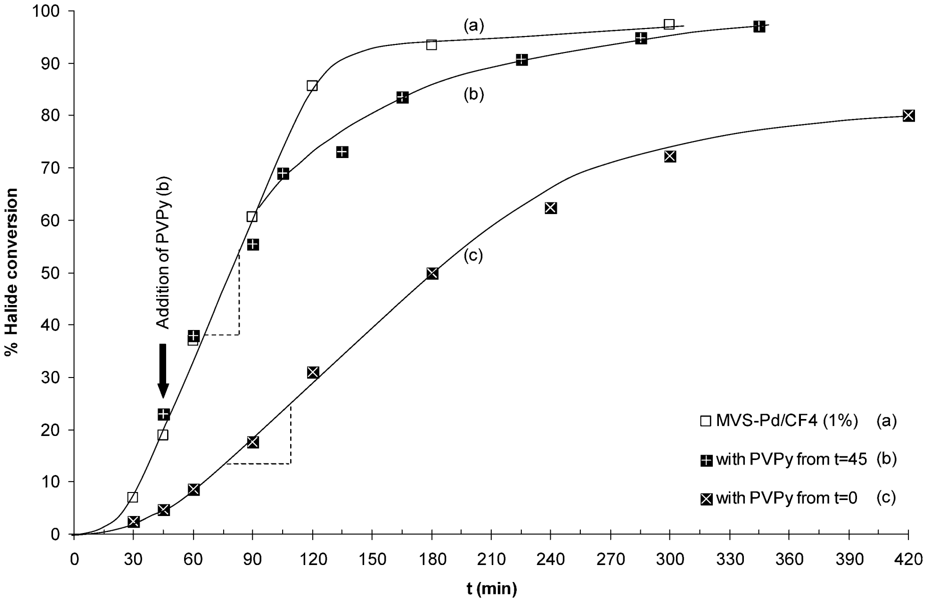


Fig. 8. Conversion vs time plots in the coupling of iodobenzene with methylacrylate over MVS-Pd/CF4 (2nd batch): (a) no PVPy added; (b) extra PVPy added at $t = 45$ min (conv. = 23%); (c) extra PVPy added at $t = 0$ (reaction mixture preheated at 100 °C for 5 min before the addition of iodobenzene).

late that in our case the amount of leached palladium was likely much lower (no leaching data were reported by Yu et al. in Ref. [5a]). The molar ratio between pyridyl functions and leached palladium should be much higher in our case, and hence the amount of palladium in the bulk liquid phase (only a fraction of the leached metal) should be much lower. It is therefore tempting to attribute to supported palladium species the residual catalytic activity observed when extra PVPy was added since the very beginning of the reaction. This would lead to the conclusion that in MVS-Pd/CF4 the contribution to the overall catalytic activity from heterogeneous catalysis is comparable to that of leached species. As for the possible nature of these species, it was not investigated in detail at this stage. However, MVS-Pd/CF4 after duty changed its color from the original black to orange-yellowish. This suggests that after being oxidized by the aryl halide, palladium is retained inside of the support as grafted Pd(II) complexes. This is in line with Choudary's observation of halo-palladium(II) species in his catalyst, after duty, supported by a layered double hydroxide [13]. The "heterogeneous" contribution to the catalytic activity, if any, might come from them rather than the surviving palladium nanoclusters. This hypothesis is supported by the absence of any homocoupling or hydrodehalogenation products at the end of the reaction, which could be expected when aryl groups are conveyed close to each other onto a permanent palladium surface, as argued above and shown by Kohler [7b].

However, further investigation is needed to prove any contribution from supported species, whatever they are. In fact, it has been shown that the activity of homogeneous ligand-less palladium catalysts increases as the overall palladium concentration in solution is lowered [25a] and that these systems are still very active at overall substrate/Pd molar ratios approaching 10^5. However, under these conditions of extreme palladium dilution, the yields achieved with a purely homogeneous system in times acceptable for practical application are too low [25a]. We could have met this condition with MVS-Pd/CF4 when extra PVPy was added. In spite of this, we still observed an appreciable reaction rate. Therefore, even if in MVS-Pd/CF4 there is no contribution from supported active species, PVPy seems to have the potential to implement a pre-catalyst, allowing an improved utilization of palladium in solution with respect to a purely homogeneous catalyst.

4. Conclusions

Palladium catalysts supported on functional organic resins are precursors of active catalysts for the Heck reaction in aprotic polar solvents (alkylamides). Like many other supported catalysts, most of them work on the basis of a metal release/recapture process. The nature of the functional groups bound to the polymer backbone affects the rate and the extent of metal leaching, which also depends on the nanocluster sizes. Therefore, different preparation procedures, yielding different metal nanocluster dimensions, lead to different catalytic performances.

As for MVS-Pd/CF4, our data show on one hand that it is not a leaching-free catalyst, but they suggest, on the other, that supported palladium species could make an important contribution to the overall catalytic activity. However, the possibility that MVS-Pd/CF4 is only the precursor of a "homeopathic" [25a] homogeneous ligand-less catalytic system cannot be ruled out yet. Whatever the nature of the PVPy-based catalyst, however, it is a very interesting and promising material: if it will be shown to be at least partially heterogeneous, optimization could lead to a leaching-free catalyst in polar aprotic solvents, based on a commercial, readily available solid support. If, on the other hand, it will turn out to be only a precatalyst, PVPy could be used to create “homeopathic,” homogeneous ligand-less catalysts useful at substrate/Pd molar ratios even higher than those currently suggested in the literature (10^3–10^4).

Acknowledgments

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