FULL PAPERS

Pd(II)-Schiff Base Complexes Heterogenised on MCM-41 and Delaminated Zeolites as Efficient and Recyclable Catalysts for the Heck Reaction

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Abstract: We present a widely applicable approach for the preparation of Pd-complexes supported on silica-based mesoporous and laminar inorganic solids (silica gel, purely siliceous and acidic MCM-41, and delaminated zeolites ITQ-2 and ITQ-6) which involves the use of the Schiff bases 2-*tert*-butyl-4-methyl-6{(*E*)-[(2*S*)-1-(1-arylmethyl)pyrrolidinyl]imino}methylphenol (aryl = phenyl, 1-naphthyl, 2-naphthyl) as anchored ligands. As an extension of our research in "recyclable catalytic systems" we report results demonstrating the reactivity and recyclability of these systems for the Heck reaction (in a biphasic mode using ethylene glycol and toluene) and Suzuki coupling under phosphine-free conditions. The complexes are insensitive to oxygen or moisture, and no change of their activity was observed when exposed to an open system during the usual operation. No palladium black was observed after an extended reaction time and no residual palladium was detected from the filtrate at the end of the reaction.

Keywords: Heck reaction; heterogenisation; immobilised; palladium; Schiff bases; Suzuki coupling

Introduction

The heterogenisation of homogeneous catalysts and their use in the production of fine chemical synthesis has become a major area of research, since the potential advantages of these materials (simplified recovery and reusability, the potential for incorporation in continuous reactors and microreactors) over homogeneous systems can have positive environmental consequences.[1,2] The majority of the novel heterogenised catalysts are based on silica supports, primarily because silica displays some advantageous properties, such as excellent stability (chemical and thermal), good accessibility, and the fact that organic groups can be robustly anchored to the surface to provide catalytic centres.

The palladium-catalysed coupling of olefins with aryl or vinyl halides, known as the Heck reaction, is a standard method for carbon-carbon formation in organic synthesis.[3] Academic and industrial interest in this reaction has increased in recent years, including the advent of an enantioselective variant,[4] the development of more active catalyst systems, the discovery of waste-free versions,[1,5] and the desire to put the vast empirical data on a sound mechanistic basis.[6] Moreover, if would be interesting to find good alternatives to the phosphines which are commonly used as ligands in the catalyst, and which are toxic and unpleasant to work with.

The commonly used palladium species in Heck's reactions are palladium acetate, palladium chloride, or preformed triarylphosphine palladium complexes.[3] However, all homogeneous catalysts present separation, regeneration and reuse problems. These problems are of environmental and economic concern in large scale-synthesis where large volumes of hazardous wastes and high production costs can be limiting factors. These problems can be minimised by carrying out the reactions using heterogeneous catalysts which can be more easily separated from the reaction mixture and recycled in successive batch operations.[7–10] We are focusing on new chiral Schiff base ligands containing pyrrolidinamino functionalities in place of one phenolic group on salen ligands [salen = (*R,R*)-*N',N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine]. The method we have developed should allow the easy synthesis of a wide variety of chiral Schiff base ligands.[11] The iminophenoxy ligands were designed to coordinate with Pd(II) and the additional amino group could be varied in order to improve the performance of the complexes in catalytic reactions.

Herein we present a very easy and widely applicable approach for the preparation of Pd complexes support-

ed on silica-based MCM-41 and laminar inorganic solids with very high specific surface (>600 m²/g), which involves the use of the Schiff bases 2-*tert*-butyl-4-methyl-6{(E)-[(2S)-1-(1-arylmethyl)pyrrolidinyl]imino}methyl-phenol (aryl = phenyl, 1-naphthyl, 2-naphthyl) as anchored ligands. One relevant feature of our catalyst is that it does not require addition of phosphines (commonly introduced into palladium-catalysed reactions) thus also improving the atom economy of the reaction.

Results and Discussion

In the last years we have developed a modular system combining functionalised ligands with different supports and linkers in order to have a systematic access to a variety of immobilised chiral catalysts.[12] We have applied here this methodology to immobilise Schiff base ligands on a mesoporous silica supports (Scheme 1), selected to encompass a wide range of topologies, such as MCM-41, ITQ-2, and ITQ-6 delaminated zeolites, and amorphous silica. With respect to the supports, both silica and MCM-41 are short-range amorphous materials containing a large number of silanol groups available for grafting. In the case of MCM-41 however, the material presents a long-range ordering with hexagonal symmetry with regular monodirectional channels of 3.5 nm diameter. On the other hand, ITQ-6 and ITQ-2 delaminated zeolites present both short- and long-range order, together with a very large, well structured external surface on which the silanol groups act as grafting centres. However, there are structural differences between the two delaminated zeolites. Indeed, in the case of the ITQ-2 there are "cup-like" apertures to the external surface with $\sim 0.8 \times 0.8$ nm dimensions, while in the case of the ITQ-6 these "cups" are less deep (~ 0.3 nm). In a previous work and by a molecular dynamics study, we have shown that there is a minimum of potential energy in the void space of the "cups" in the ITQ-2, in which the molecules that can fit have a high tendency to adsorb.[13] Taking this into account and the fact that the structured silanols are located at the borders of these "cups", one can envisage an structural model analogous to that presented by Breslow et al.[14] for cyclodextrins in which the grafted complex site is located at the border of the cyclodextrin "cup". In our case, the metal complex will be located at the border of the inorganic silicate cups. Then, one may expect that the reactant is adsorbed in the cavity of the delaminated zeolite and reacts there with the catalyst located at the border. If this model is correct, we should expect an increase in the concentration of reactants close to the catalytic active site and, consequently, an increase in the rate of the reaction should occur.

All solids were functionalised in the same manner according to the procedure shown in Scheme 1. Supported precursors, **2**-(support), were obtained by refluxing a mixture of the precursor **2** and the respective support, in toluene, for 16 hours. These anchored aldehydes reacted with an equimolar amount of (S)-(1-benzyl-2-pyrrolidinyl)methylamine, (S)-[1-(1-naphthylmethyl)-2-pyrrolidinyl]methylamine and (S)-[1-(2-naphthyl-methyl)-2-pyrrolidinyl]methylamine to afford the supported chiral Schiff ligands, **3–5**-(support), as fine powdered solids. In the ¹³C NMR spectra, the C-OH carbon signals appear at $\delta = \sim 153$ ppm, and the imine carbons appear at $\delta = 165–166$ ppm.

The heterogenised ligands reacted with palladium(II) acetate to furnish the corresponding anchored Pd complexes. The catalysts prepared present metal loading of 0.25–0.80 mmol metal/g support as determined by atomic absorption analysis (see Table 1). The spectra of diamagnetic palladium complexes show the simultaneous occurrence of two set of signals, which are related with the substituted benzaldimine entity and with the aliphatic part of the ligand. The ¹³C NMR spectra showed the signals assigned to the C=N carbon high-field shifted and C-1 at $\delta = ca.$ 162 down-field shifted confirming that metallation had occurred.

Catalysis in liquid-liquid two phase systems is generally referred to as biphasic catalysis, the catalyst is present in one phase while reactants and products are present in the other organic phase. In our case the term "biphasic" refers to the mixture of two immiscible solvents while the catalyst exists in a third phase. In this work we have studied the performance of various supported Pd complexes for Heck reactions of iodobenzene using the biphasic mixture toluene and ethylene glycol as solvent in the presence of potassium acetate.[15]

We now show the reactivity and recyclability of these systems for the Heck reaction of aryl halides (chloro-, bromo-, and iodobenzene) with olefins (styrene, diethyl itaconate and *n*-butyl acrylate) under phosphine-free conditions (Table 2). The complexes are insensitive to oxygen or moisture and no change in their activity was observed when the reaction was carried out in an open system. As expected, the bromo and iodo compounds are both active while chlorobenzene was virtually inert in our experimental conditions.

Table 1. Metal loading in the support.

Catalyst	mmol-metal/g support
3Pd-(MCM-41)	0.27
3Pd-(ITQ-2)	0.31
3Pd-(ITQ-6)	0.25
3Pd-(MCM-41) (Si/Al ≈ 15)	0.40
4Pd-(Sil)	0.46
4Pd-(MCM-41)	0.39
4Pd-(ITQ-2)	0.32
5Pd-(MCM-41)	0.51
5Pd-(ITQ-6)	0.80
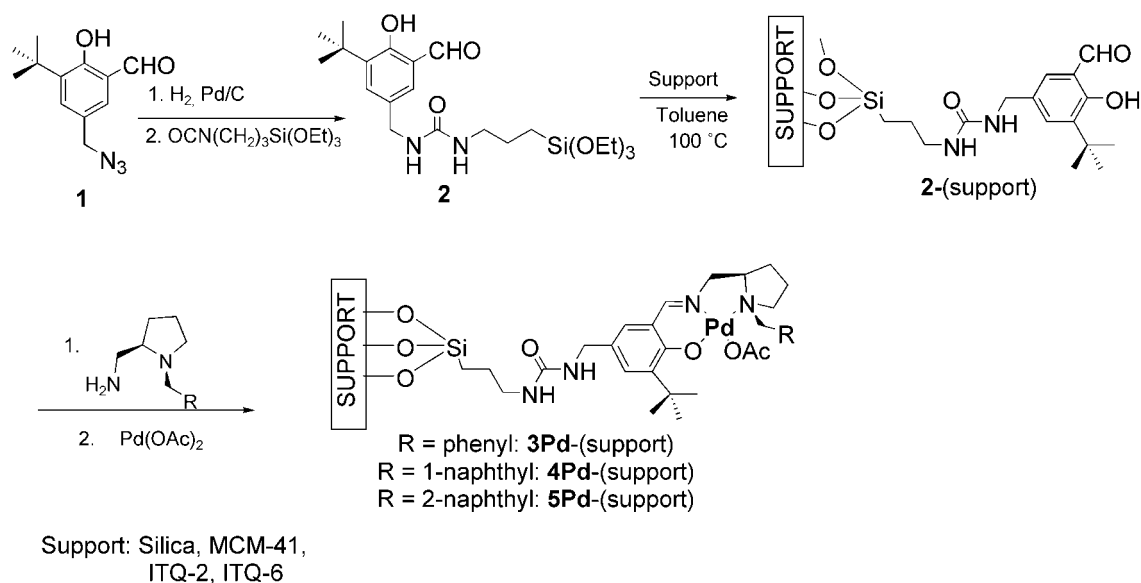
Scheme 1. Synthesis of ligands and complexes.

Among the various bases examined, 1.14 mmol of NaOAc or KOAc proved to be most suitable in combination with catalyst (<5 mol %), and use of other bases resulted in lower yields: Et$_3$N (<10%). More polar solvents than **3**, such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO) or acetonitrile were tested for this reaction, but only low conversion of the aromatic halide was achieved. The use of *N*-methylpyrrolidone (NMP) produces a clear increase in conversion and selectivity, probably due to the high solubility of the base and the intermediate salts formed in the reaction media. The problem with this solvent and the supported catalyst is the leaching of the metal (>50%) to the solution under the usual reaction conditions. On the contrary, when Heck vinylation reactions were performed in a biphasic mode using ethylene glycol and toluene (Figure 1) with 5 mol % Pd(II), and KOAc as an efficient base, high yields were achieved without the need for an extra ligand such as triphenylphosphine. This catalytic system is stable and recyclable and reaction products, catalyst and base can be easily separated. In the biphasic vinylation system, the toluene phase contains the reactants and products, while metal complex and potassium acetate are in the ethylene glycol phase. The inorganic base added is partly soluble in the ethylene glycol phase. The reaction should occur in the ethylene glycol phase and the ethylene glycol-toluene interface in which the base is partly soluble.

In Table 2 we show the catalytic performance of various supported complexes for the Heck reaction. The reaction was successful using low Pd catalyst loadings (2 – 5 mol %), but the reactions did not proceed at concentrations below 2 mol %. Analogous nickel complexes do not react under the same reaction conditions. When using the palladium complexes, no palladium black

was observed after more than 72 hours. As shown in Table 2, under the optimised conditions, the Heck-type olefination reactions of aryl halides were readily achieved with a variety of olefins.

Comparative reactions have been carried out with a homogeneous equivalent of the supported catalyst in exactly the same conditions. The initial green solution of homogeneous catalysts in *N*-methylpyrrolidone turned to red upon heating after addition of base and particles of palladium black could be seen in the flask. These observations led us to the hypothesis that palladium colloids will be generated upon addition of base to a solution of the homogeneous precursor when heating the reaction mixture.[16] Indeed, upon centrifugation of the reacted mixture we could isolate palladium particles. These isolated particles were used in a new reaction and they were catalytically inactive. The absence of reactivity is presumably due to a significant aggregation of the particles under the reaction conditions. When the filtered solution was used as catalyst, it was observed that transformation of iodobenzene does not occur.

In Figure 2 the catalytic performance of various supported Pd-complexes is shown for the reaction of iodobenzene and butyl acrylate under biphasic conditions. The similar rates observed for homogeneous and supported catalysts indicate that diffusion is not a major problem under the conditions used here, and the extended lifetime may be a feature of the Pd being tethered to the support at a low density, stopping deactivation through clustering. It is interesting to notice that while the reaction selectivity is practically not influenced by the catalyst, the activity is dominated by the support. In a first approximation, the following order of activity for the supported catalyst can be inferred from the results (after 24 hours): **4Pd**-(ITQ-2) $>$ **5Pd**-(MCM-
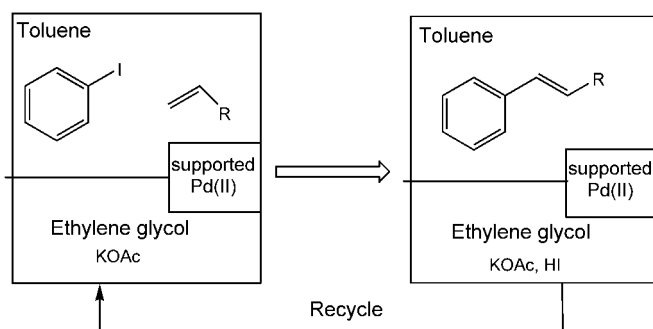
Figure 1. Heck vinylation reactions performed in a biphasic mode using ethylene glycol and toluene.

Figure 2. Catalytic performance of the Heck reaction.

41) > **4Pd**-(MCM-41) > **3Pd**-(MCM-41) > **3Pd**-(MCM-41, Si/Al = 15) > **4Pd**-(Sil). The aluminium content of MCM-41 shows only a minor influence on the conversion in the Heck model reaction investigated, indicating that there is no effective charge separation along the reaction.[17] From a preparative point of view, conversions higher than 95% were achieved after longer reaction times and 100% selectivity to *trans*-butyl cinnamate were observed irrespectively of the precursor used. The activities for diethyl itaconate were similar to those for *n*-butyl acrylate, whilst the activity for styrene was lower, and longer reaction times are needed for high conversions (5 days, 85%).

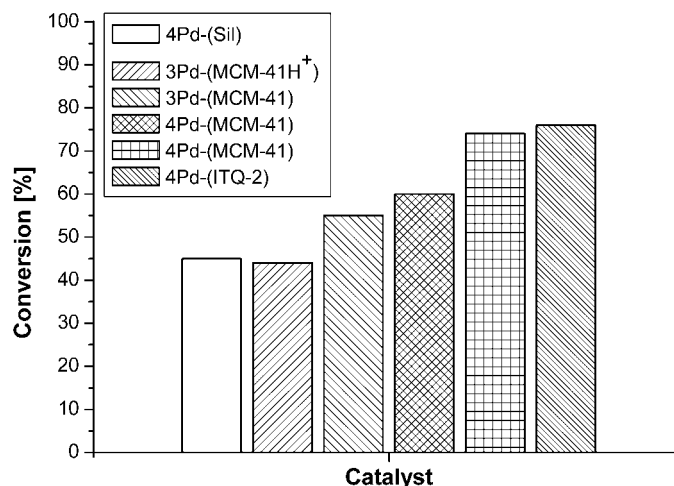When compared with commercial 5% Pd/C we found that anchored palladium complexes were more active and more stable, due to the higher dispersion of the metal and the better resistance to leaching by the reaction solution. Moreover, the recycling procedure for our catalysts is significantly easier than the standard Pd/C catalyst.

Separation, Recycling and Catalyst Reuse

The recycle experiments were made by separating the ethylene glycol phase and reusing this together with fresh toluene and KOAc (Figure 1). Since the stability of the supported complexes towards dissolution during

Table 2. The Heck reaction of aryl halides with olefins using homogeneous and supported palladium catalysts.[a]

R[1]	R[2]	Base	Solvent	Catalyst	Conv. [%][b]
Ph	H	NaOAc	NMP	**3Pd**-(ITQ-2)	45
Ph	H	NaOAc	NMP	**3Pd**-(ITQ-6)	13 (30)[d]
Ph	H	NaOAc	NMP	**5Pd**-(ITQ-6)	44
Ph	Me	KOAc	Biphasic[c]	**4Pd**-(MCM-41)	10 (35)[d]
CH$_2$CO$_2$Et	CO$_2$Et	NaOAc	NMP	**5Pd**-(ITQ-6)	39
CH$_2$CO$_2$Et	CO$_2$Et	KOAc	Biphasic[c]	**4Pd**-(Sil)	14 (30)[d]
CO$_2$Bu	H	KOAc	Biphasic[c]	**4Pd**-(Sil)	42
CO$_2$Bu	H	KOAc	Biphasic[c]	**3Pd**-(MCM-41)	55 (70)[d]
CO$_2$Bu	H	KOAc	Biphasic[c]	**3Pd**-(MCM-41) (Si/Al ≈ 15)	40
CO$_2$Bu	H	KOAc	Biphasic[c]	**4Pd**-(MCM-41)	58
CO$_2$Bu	H	KOAc	Biphasic[c]	**5Pd**-(MCM-41)	64
CO$_2$Bu	H	KOAc	Biphasic[c]	**4Pd**-(ITQ-2)	74

[a] Reactions were carried using 1 mmol of substrate and supported palladium catalyst (5 mmol %) with base (1.14 mmol) and 6 mL of solvent at 140 °C.
[b] Conversion after 24 h.
[c] Ethylene glycol/toluene.
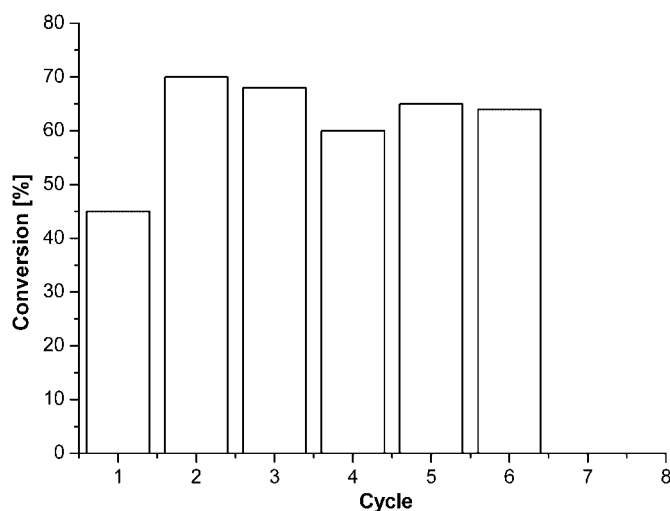[d] In parenthesis conversion after one time recycled.

Figure 3. Recycling experiments for catalyst **3Pd**-(MCM-41).

Figure 4. Effect of removing the supported palladium catalyst from the Heck reaction.

the reaction is a problem of great concern for most anchored catalysts,[18] and considering the leaching problems observed with palladium supported on polymer beads, quantitative analysis using atomic absorption spectroscopy (AAS) was employed to determine the amount of metal in the final reaction solution. We have observed (Figure 3) that the catalyst could be recycled, at least, six times without significant loss of activity. In order to check the stability of metal complexes supported on the solid matrix, we have characterised the solid before and after reaction. As can be deduced from IR, ^{13}C NMR and UV-VIS spectra the nature of supported species is very similar and the most important signals for Schiff base ligands appear in the same position after reaction.

Although extensive studies have been carried out to elucidate the true catalytic species in the heterogeneous Pd-catalysed Heck reaction, it is still unclear in many cases whether the reaction takes place on the surfaces of the solid Pd catalyst[19] or whether the active catalysts are Pd species leached out from the support, which simply acts as a reservoir of Pd.[20] Taking this into account, it is mandatory to find out if some Pd has passed into the solution. To do this, we have investigated the residual activity of the supernatant solution after separation of the catalyst. The potential leaching was studied as follows: the organic phase of a first run was separated from the solid (Pd-supported). New reagents were added to the clear filtrate, and the composition of the reaction mixture was determined by GC. This homogeneous reaction mixture was treated as a standard catalytic experiment (140 °C, 24 h). After 24 h, the composition was determined and no reaction was observed, which excludes the presence of active species in solution. Leaching of the palladium complex can also be discarded because the amount of Pd in the solid before (0.27 ± 0.02 mmol/g) and after (0.25 ± 0.02 mmol/g) the consecutive catalytic reactions was mainly unchanged. When
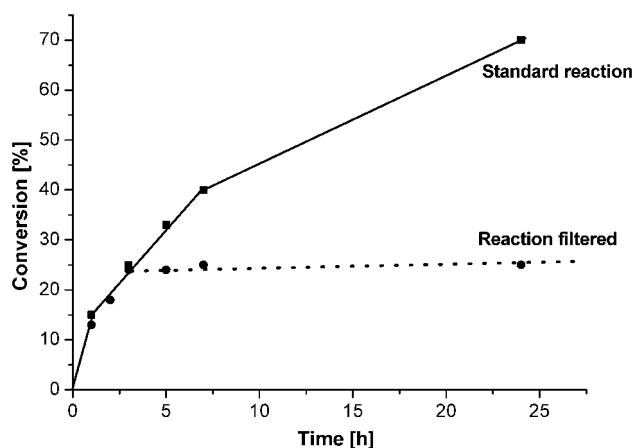
the reaction mixture was filtered through a micropore filter, no residual Pd was detected from the filtrate by ICP analysis ($<$ 1 ppm) implying that leaching of Pd from the support is negligible.

Moreover, to rule out the contribution of homogeneous catalysis in the results shown in Table 2, one reaction was carried out in the presence of the solid until the conversion was *ca.* 20% and at that point the solid was filtered off at the reaction temperature. The liquid phase was transferred to another flask and the again allowed to react, but no further significant conversion was observed (Figure 4, 23% after 24 h).[21]

An important point concerning the use of a heterogeneous catalyst is its lifetime, particularly for industrial and pharmaceutical applications of the Heck reaction. After separation and washing, the heterogeneous catalysts were used several times for the same reaction under the same conditions as for the initial run of the catalyst. We usually see an increase of activity after the first run, followed by a slight decrease of the rate due to the small amount of catalyst lost by manipulation (Figure 3).

The palladium catalysts bound on MCM-41 and delaminated zeolites have been also tested in the Suzuki reaction between phenylboronic acid and bromobenzene in xylene in the presence of potassium carbonate as the base. The optimal reaction conditions were applied to a series of catalysts and conversions $>$ 80% were obtained at 24 h. Better yields have been obtained with catalysts **5Pd**-(Sil) and **5Pd**-(MCM-41). This experiment show that these palladium supported complexes could be applied for other C−C couplings.

Conclusion

In conclusion, a novel series of mesoporous silica-supported palladium catalysts has been successfully prepared through sequential grafting of organic functional groups. The catalysts are active in Heck reactions and,

more importantly, are stable to the reaction conditions and can be recycled without loss of activity. The facts that no inert atmosphere and no additional ligands are necessary, the easy separation, and the easy availability make the supported palladium catalysts an interesting alternative to homogeneous catalysts.

Experimental Section

General Remarks

Metal complexes were prepared under dinitrogen by conventional Schlenk tube techniques. Solvents were carefully degassed before use. The silylating agent $OCN(CH_2)_3Si(OEt_3)_3$ was obtained from ABCR. C, H and N analysis were carried out by the analytical department of the Institute of Materials Science (C.S.I.C.) with a Perkin-Elmer 240C apparatus. Metal contents were analysed by atomic absorption using a Perkin Elmer AAnalyst 300 atomic absorption apparatus and plasma ICP Perkin Elmer 40. IR spectra were recorded on a Bruker IFS 66v/S spectrophotometer (range $4000-200$ cm^{-1}) in KBr pellets. High resolution ^{13}C MAS or CP/MAS NMR spectra of powdered samples, in some cases also with a Toss sequence, in order to eliminate the spinning side bands, were recorded at 100.63 MHz, 6 μs, 90^0 pulse width, 2 ms contact time and $5-10$ recycle delay, using a Bruker MSL 400 spectrometer equipped with an FT unit. The spinning frequency at the magic angle ($54^044'$) was 4 KHz.

The inorganic supports for anchoring were silica gel [Merck silica, average pore diameter 40 Å], purely siliceous MCM-41,[22] and delaminated zeolites ITQ-2 and ITQ-6.[23] In addition, Al-containing MCM-41 samples with Si/Al ratios of 15 and 50 were used as support for loading the complex.

Catalyst Preparation

The catalyst preparation (Scheme 1) involves the anchoring of organosilanes onto mesoporous silica followed by subsequent modification reactions. The organically modified silica-based mesoporous solids (silica gel, purely siliceous and acidic MCM-41, and delaminated zeolites ITQ-2 and ITQ-6) materials were prepared and completely characterised as we described previously.[24]

Synthesis of Heterogenised Terdentate Ligands

Typically, a solution of 2 mmol of the aldehyde **2** in toluene (5 mL) and 100 μL of water were added to a suspension of silica or the corresponding mesoporous solids MCM-41, ITQ-2 or ITQ-6 (1 g) in toluene (25 mL), stirred at room temperature for 30 minutes. The slurry was heated at 100 °C for 16 h and the yellow solid was filtered off and washed successively with toluene, petroleum ether, ethanol and diethyl ether. Then, a stirred slurry of 1 mmol of the corresponding anchored hydroxyaldehyde **2**-(Sil, MCM-41, ITQ-2, ITQ-6) was prepared in ethanol (10 mL) under argon at room temperature. After 10 min, 125 mg (1.1 mmol) of the amine were added and the mixture stirred for 16 hours. The mixture was allowed to cool

and the deep yellow solid was filtered off and washed thoroughly with ethanol and then with ether. The solid was dried under vacuum to afford the corresponding anchored ligands [ligand-(support)]. Only spectroscopic data for one representative member of the series are presented.[25]

3-(MCM-41): Anal. found: C 16.3, H 3.0, N 2.5%; (0.44 mmol/g). IR (KBr): $\nu = 1630$, 1557 cm^{-1} (C=N, C=O, C=C); UV-VIS: $\lambda = 224$, 264, 347, 419 nm; ^{13}C NMR (solid): $\delta = 166.60$ (*CH*=N), 160.53 (NH*C*ONH), 153.62 (*C*-OH), 136.99 (*C-6*, C_{arom}, *C-4*, *C-2*), 128.74 (C_{arom}, *C-3*, *C-5*), 66.50 (*C-2′*, CH=N*CH$_2$*), 58.98 (*CH$_2$*Ph), 53.64 (*C-5.*), 42.48 (*CH$_2$*CH$_2$CH$_2$Si, C*CH$_2$*NH), 28.40 [*C*(CH$_3$)$_3$, *C-3′*], 22.09 (CH$_2$*CH$_2$*Si, *C-4′*), 8.02 (*CH$_2$*Si).

Preparation of Supported Palladium Catalysts

Heterogenised complexes were synthesised following the general method: an ethanolic solution of Pd(OAc)$_2$ or Ni(OAc)$_2$ (0.5 mmol/15 mL) was added to a suspension of heterogenised ligand in toluene (20 mL) at room temperature. The resulting mixture was stirred under reflux for 12 h, cooled to room temperature and filtered. The solid was washed several times with ethanol, dried and filtered to afford the corresponding heterogenised complexes, complex-(support), in almost quantitative yields.[25] Spectroscopic data for one representative member are given:

3Pd-(ITQ-2): Anal. found: C 13.4, H 1.4, N 1.9, Pd 3.3%; (0.31 mmol/g). IR (KBr): $\nu = 1630-1562$ (C=N, C=O, C=C), 560 cm^{-1} (Pd-O); UV-VIS: $\lambda = 225$, 258, 289, 335, 412 nm; ^{13}C NMR (solid): $\delta = 186.92$ (OO*C*CH$_3$), 169.09 (NH*C*ONH, *C*-O-Pd), 158.65 (*C*H=N), 137.78 (*C-2*), 126.14 (C_{arom}, *C-5*, *C-3*), 119.22 (*C-6*), 65.23 (CH=N*CH$_2$*, *C-2′*), 62.56 (*CH$_2$*Ph), 57.83 (*C-5′*), 46.66 (*CH$_2$*CH$_2$CH$_2$Si, C*CH$_2$*NH), 34.04 [*C*(CH$_3$)$_3$], 28.95 [C(*CH$_3$*)$_3$, *C-3′*], 24.09 (*C-4′*, CH$_2$*CH$_2$*CH$_2$Si), 17.30 (OO*C*CH$_3$), 12.45 (*CH$_2$*Si).

Catalyst Testing

Heck reaction: In a typical experiment, catalyst (0.03 mmol, 5%) was suspended in a mixture of ethylene glycol and toluene (1:1, 6 mL). Then iodobenzene (1 mmol), n-butyl acrylate (1.14 mmol), and potassium acetate (1.14 mmol) were added with stirring. The mixture was refluxed and the reaction progress was monitored by gas chromatography.

Preparative experiment: Following the general method, when the reaction was finished the toluene phase was separated and the product was obtained by solvent evaporation.

Typical Suzuki reaction: Catalyst (0.3 mmol, 5%) was suspended in o-xylene and benzeneboronic acid (10 mmol), bromobenzene (15 mmol), aqueous potassium carbonate (20 mmol) were added. The reaction mixture was then heated at 143 °C and its progress followed by GC.

Acknowledgements

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