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Nanosized metallic particles embedded in silica and carbon aerogels as catalysts in the Mizoroki–Heck coupling reaction

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We have prepared silica, organic, and carbon aerogels doped with metallic Ni and Pd through sol-gel processes. Silica aerogel nanocomposites have been synthesized by impregnation, with $Ni(acac)_2$ or $Pd(acac)_2$, of the silica wet gels followed by ethanol supercritical drying. Organic aerogels were prepared by sol-gel copolymerization of formaldehyde with the potassium salt of 2,4-dihydroxybenzoic acid, followed by ion exchange with either $Ni(NO_3)_2 \cdot 6H_2O$ or $Pd(OAc)_2$ and CO_2 supercritical drying. No special reduction step was needed. Organic aerogels were further carbonized to obtain carbon aerogels. Pd organic and carbon aerogels containing 20–40% palladium nanoparticles are good catalysts for the Mizoroki–Heck reaction.

Introduction

Nowadays, new materials prepared by sol-gel processes are of great interest in materials science. Aerogels form a new class of solids showing potentialities for a range of applications.[1] The most common aerogels are inorganic, usually derived from sol-gel polymerization of tetraalkoxysilanes followed by supercritical drying. Moreover, polycondensation of certain organic monomers can be used to prepare organic aerogels.[2] For example, polycondensation of resorcinol with formaldehyde affords gels that can be supercritically dried to form organic aerogels which, once pyrolyzed, give rise to carbon aerogels. For both types of aerogels, the drying of the gels is carried out by supercritical solvent evacuation since pore collapse normally occurs when drying under ambient conditions. In this way highly porous materials are obtained.

Moreover, the sol-gel process allows the preparation of metal nanoparticles. The best way to protect metallic nanoparticles from air-oxidation is encapsulation in inert matrices as fullerenes, or oxides such as alumina,[3] titanium oxide[4] or silica.[5]

We are interested in the field of heterogeneous catalysis and we have previously reported that ferrihydrite–silica aerogels, having high specific surface and high porosity, are recoverable and reusable catalysts for some classical organic reactions.[6] To extend the scope of aerogels in catalysis we have turned our attention to the preparation of aerogels doped with Ni and Pd.

Metal-doped carbon aerogels are well-known.[7] They have been prepared by Baumann *et al.*[8] by sol-gel polymerization of resorcinol derivatives containing ion-exchange moieties. The method was shown to be effective to uniformly incorporate metal ions [Co(II), Cu(II) and Ni(II)] into the aerogel matrix. The gels were dried with $scCO_2$ to form the aerogels that were then pyrolyzed. Others have used a similar methodology to obtain Fe, Co, Ni, Cu, Ti, Cr, Mo, and W doped organic aerogels.[9] Adapting the methods described in ref. 8 and 9, Ni– and Pd–carbon aerogels have been prepared.[10]

With respect to metal-doped silica aerogels most of the examples describe the synthesis of xerogels. In reference to nickel, some composites of crystalline nickel and amorphous silica have been prepared from tetraethoxysilane (TEOS) and $Ni(NO_3)_2 \cdot 6H_2O$. The dried gels were submitted to high temperature in a reducing atmosphere to avoid formation of nickel oxide.[11,12] Schubert *et al.* have reported the synthesis of Ni–SiO_2 catalysts *via* sol-gel processing of $Ni(OAc)_2 \cdot 4H_2O$, TEOS and $(EtO)_3Si(CH_2)_3NHCH_2CH_2NH_2$. The solid xerogel was dried and then reduced in a flow of hydrogen at temperatures between 773 and 932 K.[13] In this article the authors comment on the drop of catalytic activity when the materials are reduced above a certain temperature (strong metal–support interaction phenomenon). Another approach is based on a solid state exchange reaction induced by ball milling followed by a reduction treatment in H_2 flux.[14] Alumina–silica gels have also been prepared from nickel chloride and dextrose; nickel chloride is reduced by *in situ* generated hydrogen.[15] As far as we know, the only reference on aerogels themselves corresponds to the preparation of some inorganic oxide matrices, containing metallic nickel formed by $Ni(OAc)_2 \cdot 4H_2O$ reduction in an autoclave with H_2 before removing the solvent under hypercritical conditions.[16]

For incorporating palladium in silica aerogels, in most cases the metal is introduced in the initial solution as a salt [*e.g.* $Pd(OAc)_2$, $PdCl_2$ *etc.*].[17] Recently Howdle[18] described a new preparation of palladium–aerogel nanocomposites based on the use of supercritical CO_2 in an autoclave. In most cases a reduction process (H_2 at high pressure) is needed to obtain Pd(0).

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In this paper we describe the results obtained in the preparation of Ni- and Pd-doped organic and inorganic aerogels and their use as catalysts in C–C coupling reactions. No reduction step is required to obtain metallic particles of Ni(0) and Pd(0).

Experimental

Ni- and Pd-doped silica aerogels

Different nanocomposite silica aerogels were synthesized using anhydrous Ni(acac)$_2$ and Pd(acac)$_2$ as metal sources. In all cases tetraethoxysilane (Aldrich 98%) was employed as the silica source. The silica wet gels were prepared in a two step acid–base catalyzed sol-gel process. Then, impregnation of wet gels was carried out.[19]

Typical experimental procedure. Prepolymerized tetraethoxysilane was obtained by the reaction of tetraethoxysilane (Aldrich 98%, 61 mL) and a sub-stoichiometric amount of water (4.9 mL) in the presence of an acid catalyst (0.2 mL of 1 M HCl) in ethanol (61 mL). After one month at -25 °C a viscous fluid was obtained, 10 mL of which were re-dissolved in ethanol (44 mL) and aqueous ammonia (15 mL, 0.05 M). Gels were formed within 4 days. The gels were then washed in pure ethanol to remove water and impregnated only once with a saturated ethanolic solution of anhydrous Pd(acac)$_2$ or Ni(acac)$_2$ for 4 days. The samples were dried with scEtOH in an autoclave (p = 150 bar and T = 260 °C). Leaching during supercritical drying was not evaluated.

Ni- and Pd-doped organic and carbon aerogels

Typical experimental procedure. A suspension of 2,4-dihydroxybenzoic acid (2.9 g, 18.8 mmol) in distilled water (100 mL) was treated with K_2CO_3 (1.3 g, 9.4 mmol) under vigorous stirring. The suspension became clear after 0.5 h, when all the acid was neutralized. Formaldehyde (3.0 g, 37 wt%, 37 mmol) was then added to the solution, followed by the catalyst K_2CO_3 (26 mg, 0.19 mmol). The clear solution was poured into glass moulds that were then sealed. The mixture was allowed to cure for 24 h at room temperature, and 96 h at 70 °C. Next, the gels were first washed with acetone and then soaked in a 0.1 M aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ or Pd(OAc)$_2$ in acetone for 24 h; this procedure was repeated three times. Finally the gels were washed with acetone, dried with supercritical CO_2 and pyrolyzed at 1050 °C under N_2 to afford carbon aerogels. The Pd–organic aerogels were not pyrolyzed.

The materials were characterized by X-ray diffraction (XRD) with a D5000 Siemens X-ray powder diffractometer using Cu$_{K\alpha}$ incident radiation. Transmission electron microscopy (TEM) observations and selected area electron diffraction patterns were performed using a JEOL-JEM-2010 microscope operating at 200 keV. Surface area determinations were carried out following the BET (Brunauer–Emmett–Teller) method with a ASAP-2000 surface area analyzer (Micromeritics Instruments Corp.).

Mizoroki–Heck reaction

Typical experimental procedure. Ethyl acrylate (2 ml, 18 mmol), iodobenzene (0.7 ml, 6 mmol), and triethylamine (1.7 ml, 12 mmol) were dissolved in 20 ml of acetonitrile. Then, 0.028 g (0.12 mmol, 2 mol%) of **Pd–carbon (2)** aerogel were added to the mixture and the reaction was carried out under reflux and mechanical stirring during 47 h. The solution was decanted and the aerogel washed several times with acetonitrile. The combined solvent extracts were evaporated, the residue was dissolved in CH_2Cl_2 and the solution was washed with aqueous Na_2CO_3 and a saturated solution of NaCl. The organic extract was evaporated to afford ethyl *trans*-cinnamate, **5**, as an oil (0.586 g, yield = 90%). ^{1}H NMR (CDCl$_3$, 250 MHz) δ: 7.69 (d, J = 16 Hz, 1H), 7.52 (m, 2H), 7.37 (m, 3H), 6.43 (d, J = 16 Hz, 1H), 4.26 (q, J = 7 Hz, 2H), 1.33 (t, J = 7 Hz, 3H). ^{13}C NMR (CDCl$_3$, 62.5 MHz) δ: 166.9, 144.5, 134.4, 130.1, 128.8, 127.9, 118.2, 60.4, 14.2. IR (ATR, cm^{-1}): 2981, 1708, 1635, 1310, 1167, 765.

***trans*-1,2-Diphenylethylene, 6.** Mp: 116–120 °C. ^{1}H NMR (CDCl$_3$, 250 MHz) δ: 7.50 (m, 4H), 7.28–7.40 (m, 6H), 7.14 (s, 2H). ^{13}C NMR (CDCl$_3$, 62.5 MHz) δ: 137.1, 128.5, 127.4, 126.3. IR (ATR, cm^{-1}): 3023, 2964, 1946, 1879, 1811, 1752, 1600, 1490, 1447, 958, 758, 686.

***trans*-4-Phenyl-3-butene-2-one, 7.** Mp: 35–39 °C. ^{1}H NMR (CDCl$_3$, 250 MHz) δ: 7.53 (m, 2H), 7.50 (d, J = 16 Hz, 1H), 7.40 (m, 3H), 6.70 (d, J = 16 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (CDCl$_3$, 62.5 MHz) δ: 198.1, 143.1, 134.1, 130.2, 128.0, 128.7, 126.8, 26.2. IR (ATR, cm^{-1}): 3059, 2999, 1678, 1600, 1448, 1359, 1168, 976, 749, 690.

Products **5–7** were compared with authentic, commercially available samples.

Results and discussion

By sol-gel synthesis, the host matrix is formed as the result of hydrolysis–condensation reactions from an alkoxide, water, a mutual solvent, and a catalyst.[20]

Silica aerogels containing nickel nanoparticles were obtained by sol-gel processing of Si(OEt)$_4$ followed by impregnation with Ni(acac)$_2$ and supercritical EtOH drying. The material prepared (**Ni–SiO$_2$**, Table 1) contained 6 wt% of elemental nickel and possessed a BET surface area of 860 m^2 g^{-1}. Its powder X-ray diffraction pattern was characteristic of metallic fcc-Ni, no nickel oxide being observed in the XRD analysis (Fig. 1) although no special reduction process was carried out during the drying of the materials. Probably, scEtOH acted as the reducing agent.

The transmission electron microscopy (TEM) image of a **Ni–SiO$_2$** sample (Fig. 2) shows well-defined spherical particles dispersed in the silica matrix with a certain degree of homogeneity. The mean diameter of the nanoparticles determined by TEM is about 14 ± 2 nm, close to the calculated value from the Scherrer equation.

Silica aerogels (825 m^2 g^{-1}) containing 3.7% of palladium nanoparticles were obtained by the same method. The powder X-ray diffraction (XRD) pattern obtained for the **Pd–SiO$_2$** aerogel was characteristic of the metallic fcc-Pd phase (Fig. 1). No reduction step was used in the preparation of this nanocomposite. It has been previously assumed by some authors that during the drying process in the autoclave the EtOH at high temperature is responsible for the reduction of the Pd^{2+}.[17]

Table 1 Synthesis features and characteristics of silica aerogels

Material	Metal source	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Density (g cm^{-3})	Metal (%)	Mean particle size (nm)	XRD phase
SiO$_2$	—	890	0.4	0.04	—	—	
Ni–SiO$_2$	Ni(acac)$_2$	860	1.8	0.06	6.0	14 ± 2	fcc-Ni
Pd–SiO$_2$	Pd(acac)$_2$	825	1.6	0.05	3.7	39 ± 6	fcc-Pd

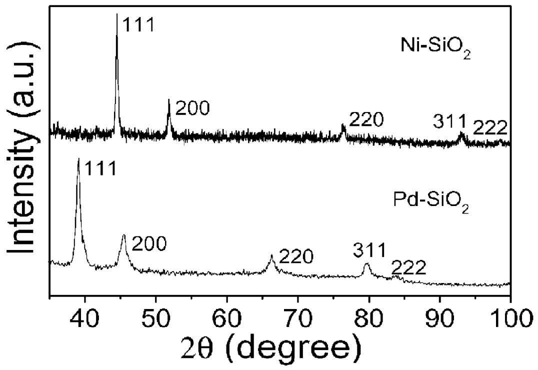


Fig. 1 XRD patterns of **Ni–SiO$_2$** and **Pd–SiO$_2$**.

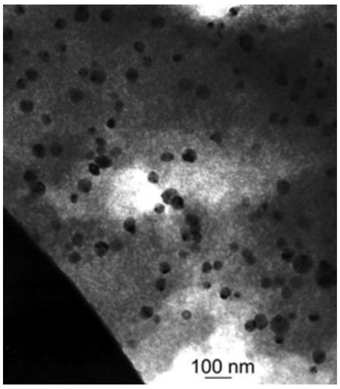


Fig. 2 TEM image corresponding to **Ni–SiO$_2$**.

Organic and carbon aerogels were prepared using the method described by Baumann.[8b] The authors comment on the fact that the metal particles are formed by reduction of the M^{2+} ions during pyrolysis of the organic aerogels.[8b] We first used TEM to examine the morphology of the Ni-doped carbon aerogel. The TEM image showed the presence of aggregates and the corresponding X-ray diffraction pattern was characteristic of metallic fcc-Ni. However, a small amount of the fcc-NiO phase was also detected (Table 2 and Fig. 4).

Curiously enough, the micrograph of the precarbonized material **Pd–organic (3)** having 21 wt% of Pd (Table 2, Fig. 3) showed particles with diameters between 6–10 nm. Electron diffraction patterns of samples of **Pd–organic (2)** and **(3)** were also obtained. Similar results were observed in both cases. As an example see in Fig. 3 the results for **Pd–organic (2)**. The diffraction rings in Fig. 3(d) can be ascribed to the (111), (200), (220), and (311) crystallographic planes of the fcc-Pd. Therefore, in the case of Pd-doped organic aerogels, metal particles were formed before the pyrolysis process, even though the XRD pattern is characteristic of an amorphous material (Fig. 4). The X-ray diffraction pattern for the **Pd–carbon (2)** aerogel (Fig. 4), after pyrolysis at 1050 °C, shows the expected crystallinity of the Pd(0) nanoparticles.

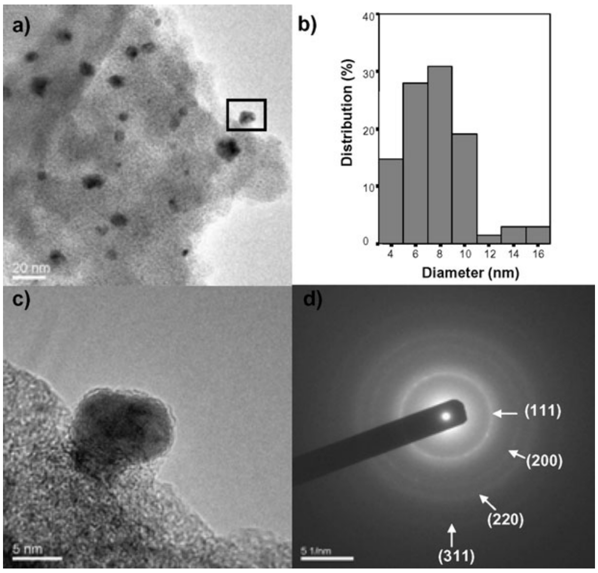


Fig. 3 (a) TEM image of **Pd–organic (3)**; (b) particle size distribution of **Pd–organic (3)**; (c) TEM close-up of the framed particle in image (a); (d) electron diffraction of **Pd–organic (2)**.

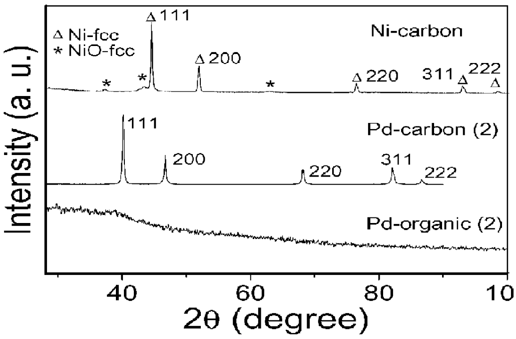


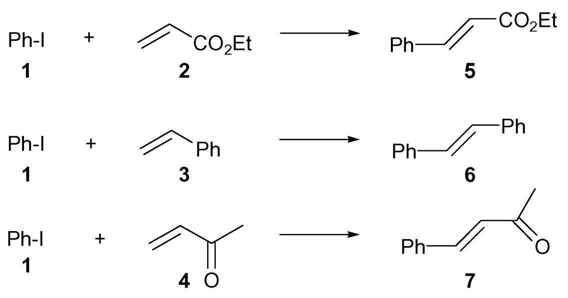
Fig. 4 XRD patterns of **Ni–carbon**, **Pd–carbon (2)** and **Pd–organic (2)**.

Some of these Ni(0)- and Pd(0)-containing materials were tested as catalysts in Mizoroki–Heck reactions (Scheme 1, Table 3). For all the Mizoroki–Heck reactions we used 2 mol% palladium with respect to the limiting reagent and triethylamine as a base in refluxing CH_3CN. Materials containing Ni(0) nanoparticles were inert as catalysts. For Pd-doped aerogels better results were obtained for **Pd–organic (3)**, having smaller Pd(0) particle size (8 nm), than for **Pd–carbon (2)** aerogel (particle size 19 nm). In the reactions of iodobenzene with ethyl acrylate and with styrene the Pd–organic aerogel is more efficient in terms of reactivity. However, from the point of view of reutilization, the Pd–carbon aerogel gave better results as the reaction was carried out four consecutive times with the same batch of aerogel without loss of activity. On the contrary, the **Pd–organic (3)** aerogel showed a slight decrease in

Table 2 Synthesis features and characteristics of carbon aerogels

Material[a]	Metal precursor	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Density (g cm^{-3})	Metal (%)	XRD	Mean particle size (nm)
Organic	—	280	1.3	0.37	—	Amorphous	—
Carbon	—	514	1.5	0.43	—	Amorphous	—
Ni–carbon	$Ni(NO_3)_2 \cdot 6H_2O$	572	1.1	0.59	19	fcc-Ni, fcc-NiO	Aggregates
Pd–carbon (1)	$Pd(OAc)_2$	408	0.8	0.88	46	fcc-Pd	27 ± 8
Pd–carbon (2)	$Pd(OAc)_2$	422	0.9	0.85	35	fcc-Pd	19 ± 4
Pd–organic (2)	$Pd(OAc)_2$	464	2	0.27	Not evaluated	Amorphous	12 ± 7
Pd–organic (3)	$Pd(OAc)_2$	386	1.4	0.26	21	Amorphous	8 ± 2

[a] The numbers in parentheses indicate different batches.



Scheme 1 Mizoroki–Heck reactions tested.

Table 3 Results for Heck reactions shown in Scheme 1

Catalyst	Olefin	Time (hours)	Product	Yield^a (%)
Pd–SiO$_2$ (1)	**2**	5/4 days	**5**	70/64
Pd–carbon (1)	**2**	47/41/44/18/120	**5**	90/81/70/99/12
Pd–carbon (2)	**2**	24/24/25/25/24	**5**	a
Pd–organic (3)	**2**	9/15/23	**5**	a
Pd–carbon (1)	**3**	7 days	**6**	79
Pd–carbon (2)	**3**	3	**6**	70
Pd–organic (3)	**3**	15	**6**	a
Pd–carbon (2)	**4**	30	**7**	90
Pd–organic (3)	**4**	50	**7**	a

^{a} Quantitative conversion by CLC chromatography.

activity in the second cycle (Table 3). Analysis of the crude reaction mixture for the first reaction indicates a leaching of 2% and 3% of the palladium present in **Pd–organic (3)** and **Pd–carbon (2)** aerogels, respectively. The **Pd–SiO$_2$** aerogel was less active and the analysis of the crude reaction mixture showed a leaching of 11% of the metal. As we have mentioned, the synthesis of the organic and carbon aerogels was based on the use of a resorcinol derivative containing an ion exchange moiety that could be polymerized using sol-gel techniques. As a result, each repeating unit of the organic polymer contains a binding site for the metal ions, securing a uniform dispersion of the dopant metal. A high dispersion of the active sites maximizes the contact of the catalyst with the reactants and can explain the difference in catalytic activity found between organic and inorganic Pd aerogels. In the cases of the Mizoroki–Heck reactions of iodobenzene with styrene and with 3-buten-2-one good results were obtained (Table 3) although the catalysts cannot be reused without decrease of activity. Polymerization of the styrene and 3-buten-2-one inside the active sites of the aerogel could be an explanation for the decreased activity.

The Mizoroki–Heck reaction catalyzed by palladium on solid support has recently attracted a great deal of attention.[21] More recently some silica gels have been prepared as supports for catalysts of the Mizoroki–Heck reaction.[22] However, in general carbon supports seem to give better results than silica.[23–25]

Conclusion

Different organic and inorganic aerogels containing Ni and Pd nanoparticles have been prepared through sol-gel processes. The materials were fully characterized. Nanosized metallic Pd nanoparticles were formed even in precarbonized Pd–organic aerogels. In no case were deliberate reduction steps necessary. We have also demonstrated that organic and carbon aerogels doped with Pd are good catalysts for the Mizoroki–Heck reaction. Carbon aerogels can be reutilized several times. Our results hold promise although require further development.

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