Highly dispersed nickel and palladium nanoparticle silica aerogels: sol–gel processing of tethered metal complexes and application as catalysts in the Mizoroki–Heck reaction

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Highly dispersed Ni and Pd silica aerogels were prepared through sol–gel processes. They have been synthesized by tethering the metal to the silica matrix with the use of the complexing silanes AEAPTS [*N*-(aminoethyl)aminopropyl]trimethoxysilane or TRIAMIN [*N*-((aminoethyl)aminoethyl)aminopropyl]trimethoxysilane. The gels were dried with $scCO_2$ to afford the aerogels. High metal dispersion and small particle sizes were observed through HRTEM and XRD measurements. The organic groups were removed by oxidation and/or pyrolysis. The Pd reduced aerogels containing 15–17% of palladium are good recoverable catalysts in the Mizoroki–Heck reaction.

Introduction

Silica aerogels are a group of extremely light and porous solid materials obtained through sol–gel processes followed by removing solvent from the wet gels at supercritical conditions of the solvent.[1] One of the striking properties of aerogels is the large surface area. In addition, metallic nanoparticles or metal-oxide nanoparticles can be placed in aerogels and be used as heterogeneous catalysts. We have previously prepared silica aerogel–iron oxide nanocomposites which were active as catalysts in conjugate additions[2] and palladium-doped organic and carbon aerogels that were good recoverable catalysts for Mizoroki–Heck reactions.[3] Moreover europium-containing organic gels have been proved to be efficient as recoverable catalysts in Michael additions.[4]

In sol–gel processing of metal–silica nanocomposite aerogels the control of homogeneity is not trivial. The difference in chemical properties between the metal salt, used as the metal precursor, and the most common silica precursors (for example TEOS) is evident. There are many reaction parameters that differently influence hydrolytic polycondensation of each precursor in a sol–gel process of a multi-precursor system. Two of the challenges are the control of the metal particle size and the homogeneity of the metal distribution. A general approach to control dispersion of the metal compound during sol–gel processing is to use the approach of tethering the metal to the gel matrix. Some of us have previously described[5] the use of organofunctional alkoxysilanes of the type $(CH_3O)_3Si(CH_2)_3A$, in which A is a group capable of coordinating to metal ions. The advantage of this method is that a two-component system is transformed in a single precursor.[6] The solid xerogels were then calcined and reduced. However, it has never been attempted to prepare aerogels by this approach.

Our interest in the fields of aerogels and catalysis prompted us to explore this methodology in the synthesis of aerogels. Therefore, the goal of this work was to obtain highly dispersed small nanoparticles of Ni and Pd embedded in silica aerogels, following the organosilane single-source method, which could be used in the Mizoroki–Heck reaction. The use of palladium on solid supports as catalysts for this reaction has recently attracted a great deal of attention.[7] Diverse palladium silica based supports have been used.[8] Recent results show that the Heck coupling can be induced by palladium acetate immobilized in reversed phase silica gel with the aid of an ionic liquid.[9] However, carbon supports[10] gave in general better results than silica supports, including palladium supported in carbon nanotubes.[10a]

Experimental

Silica aerogel nanocomposites

Different nanocomposite silica aerogels were synthesized using $Ni(OAc)_2$ and $Pd(OAc)_2$ as metal sources. In the first step, the metal complexes $[Pd(AEAPTS)_2]^{2+}$, $[Pd(TRIAMIN)_2]^{2+}$, $[Ni(AEAPTS)_2]^{2+}$ and $[Ni(TRIAMIN)_2]^{2+}$ were formed by reaction of nickel or palladium acetate with 2 molar equivalents of *N*-[(aminoethyl)aminopropyl]trimethoxysilane (AEAPTS) or [*N*((*N*-aminoethyl)aminoethyl)aminopropyl]trimethoxysilane (TRIAMIN). In the second step, tetraethoxysilane (TEOS) was added as the silica source. Sol–gel processing of the mixtures resulted in different gels that were dried with $scCO_2$ to afford the aerogels.

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Typical experimental procedure

4 mmol of the metal acetate ($Ni(OAc)_2$ or $Pd(OAc)_2$) were suspended in 50 ml of water-free ethanol, and 8 mmol of AEAPTS (1.78 g, series a) or TRIAMIN (2.24 g, series b), and the solution was stirred until the metal salt was dissolved. Then 5 g (24 mmol) of TEOS and 16.25 ml of 0.2 M aqueous NH_3 were added. The reaction mixture was stirred and then poured into plastic moulds that were sealed. The mixture was allowed to cure for 4 days at room temperature. Next, the gels were washed with ethanol and dried with supercritical CO_2.

Some of the aerogels were first transferred into a ceramic boat, placed into an oven and heated to 550 °C (heating rate 10 °C min^{-1}) during 60 min (calcination or oxidation process). Then they were reduced by placing the oxidized samples in a quartz tube, heating to 550 °C (heating rate 10 °C min^{-1}) in a stream of hydrogen and holding for 2 h.

Other aerogels were directly reduced without prior calcination. The materials were characterized by X-ray diffraction (XRD) with a D5000 Siemens X-ray powder diffractometer using Cu-Kα 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.). Thermal analyses were performed on Netzsch TG209c and Shimadzu DSC-50 apparatus.

Mizoroki–Heck reaction

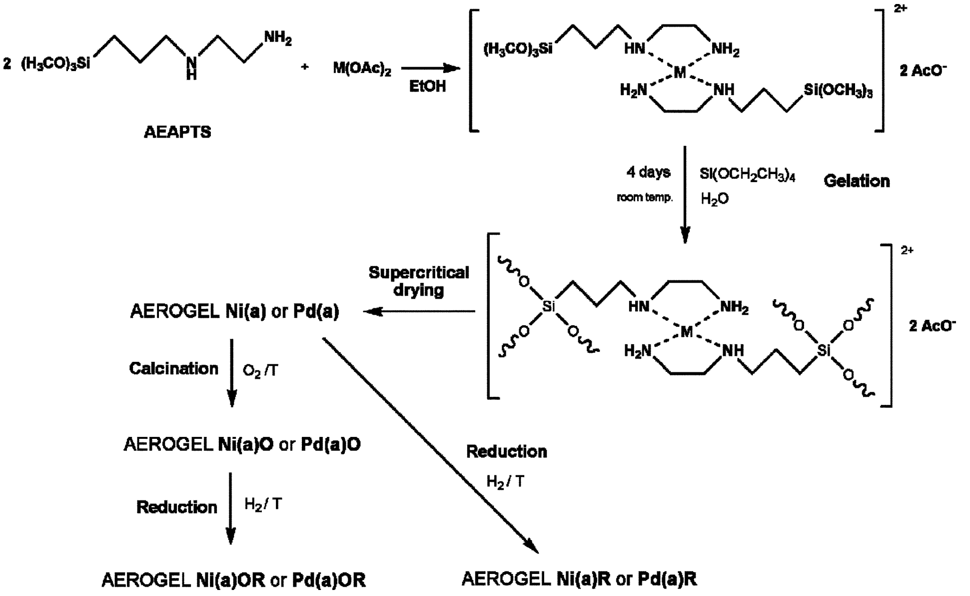
Typical experimental procedure. Ethyl acrylate (1.5 ml, 13.5 mmol), iodobenzene (0.5 ml, 4.5 mmol) and triethylamine (1.25 ml, 9 mmol) were dissolved in 15 ml of acetonitrile. Then, 0.0588 g (0.09 mmol, 2% molar) of **Pd(a)R** aerogel were added to the mixture and the reaction was carried out under reflux and mechanical stirring during 8 h, when no signal of iodobenzene appears in the GLC chromatography. The solution was decanted and the aerogel washed several times with acetonitrile. The combined solvent extracts were evaporated and 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 (yield = 99%).[3] ^{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[3].** 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[3].** 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, 128.7, 128.7, 126.8, 26,2. IR (ATR, cm^{-1}): 3059, 2999, 1678, 1600, 1448, 1359, 1168, 976, 749, 690.

Results and discussion

Different Ni and Pd silica aerogel nanocomposites were prepared following the method previously reported by some of us for the preparation of xerogels.[5c] The preparation of the aerogels included the following steps (Scheme 1): (i) *in situ* preparation of the metal complexes by reaction of the metal salt with the amino-substituted organo(alkoxy)silane. (ii) Addition of the $Si(OR)_4$ as the network former and aqueous NH_3 to start the sol–gel reactions. (iii) Drying of the obtained wet gels with $scCO_2$. The samples are designated as **M(*x*)**, where **M** is the chemical symbol of the metal, and ***x*** is the series level



Scheme 1 Preparation of different Ni and Pd aerogel nanocomposites (example for series a).

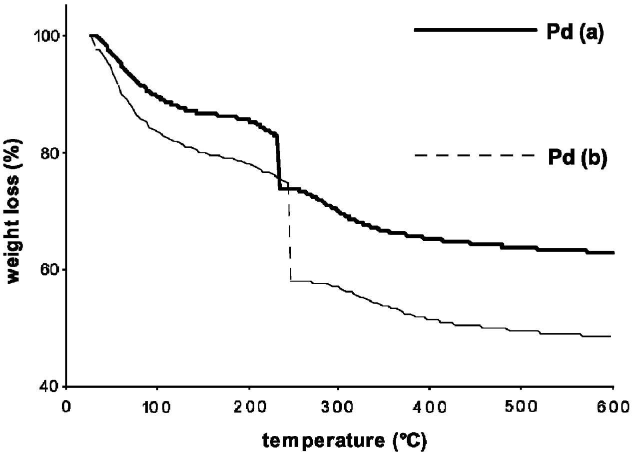


Fig. 1 TGAs of the aerogels **Pd(a)** and **Pd(b)**.

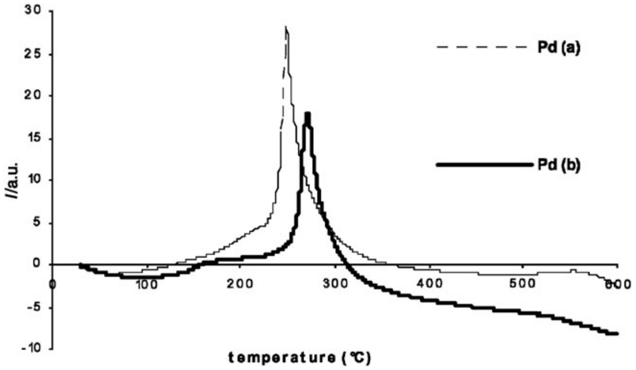


Fig. 2 DSC of the aerogels **Pd(a)** and **Pd(b)**.

depending on the complexing organo(alkoxy)silane (AEAPTS series **a**; TRIAMIN series **b**). Moreover, to study the influence of the complexing organo(alkoxy)silane on the properties of the composites, a third series of samples (series **c**) was prepared by using the same metal salts and TEOS but with no complexing organo(alkoxy)silane added. The materials of the three series exhibited differences in their gelation behavior.[5c] No gelation was achieved in the case of the **Ni(c)** (sol–gel processing of $Ni(OAc)_2$/TEOS mixtures). For **Pd(c)**, a heterogeneous gel was formed and an accumulation of the metal salt on the surface of the gel was clearly observed. On the contrary, when AEAPTS and TRIAMIN were employed, which contain the strongly coordinating ethylenediamine or diethylenetriamine groups, homogeneous gels were obtained.

The **M(a)** and **M(b)** aerogels were calcined in air to remove organic groups and to obtain metal oxide/silica aerogel nanocomposites **Ni(a)O** and **Pd(b)O** (Scheme 1). The letter **O** after **M(*x*)** indicates that the samples were oxidized. The TGAs of the aerogels denoted the temperature of the thermal degradation of the organic groups. The TGAs of **Pd(a)** and **Pd(b)** are shown in Fig. 1. The weight loss in **Pd(b)** was higher due to the larger proportion of organic groups. The TGAs of Ni xerogels materials were previously documented[5c] and similarly we decided to calcine the aerogels in air at T = 550 °C. The corresponding DSC curves of the aerogels **Pd(a)** and **Pd(b)** (Fig. 2) showed the temperature at which the exothermic pyrolysis and/or thermolysis reactions took place.

Reduction of all these materials resulted in metal/silica aerogel nanocomposites (Scheme 1). These samples were designated as **M(*x*)OR**. The letters **OR** were added after **M(*x*)** to indicate that the samples were oxidized and then reduced.

One of the goals of our previous work on metal oxide or metal/SiO_2 nanocomposites by the single-source method had been to obtain carbon-free materials. For this reason, the xerogels were calcined prior to reduction to remove the organic groups. For an application as catalysts in organic reactions, the presence of organic groups may not be detrimental. We therefore also prepared aerogels, designed with the letters **R** after **M(*x*)**, where the oxidation step was omitted. In oxidized/reduced aerogels **M(*x*)OR** the organic groups were removed by pyrolysis reactions. In contrast, in the only reduced aerogels **M(*x*)R** the organic groups are partially retained.

The nitrogen absorptions measurements showed that in all the aerogels the shape of the adsorption isotherm was of type II, characteristic of macroporous solids. In general, when the aerogels were calcined and then reduced, (**M(*x*)OR**), a large percentage of micropores were created and this resulted in an increase in porosity and specific surface area (Table 1). We have previously observed this behaviour in xerogels.[5c] Moreover, the aerogels directly reduced also presented an increase

Table 1 Synthesis features and characteristics of aerogels

Material	Metal source	Surface area/m^2 g^{-1}	Pore volume/cm^3 g^{-1}	Density/ g cm^{-3}	Metal (%)	XRD phase	Mean particle size[a]/nm
Ni(a)	$Ni(OAc)_2$	441	1.8	0.09	—	Amorphous	—
Ni(a)R	$Ni(OAc)_2$	575	3.7	0.1	—	fcc-Ni	1.7
Ni(a)OR	$Ni(OAc)_2$	393	1.9	0.13	—	fcc-Ni	12.3
Ni(b)	$Ni(OAc)_2$	439	1.3	0.27	—	Amorphous	—
Ni(b)R	$Ni(OAc)_2$	756	2.8	0.7	—	fcc-Ni	2.5
Ni(b)OR	$Ni(OAc)_2$	515	1.6	0.5	—	fcc-Ni	2.3
Pd(a)	$Pd(OAc)_2$	516	1.7	0.4	11.4	Amorphous	1.3[b]
Pd(a)R	$Pd(OAc)_2$	690	2.0	0.4	16.3	fcc-Pd	1.4
Pd(a)OR	$Pd(OAc)_2$	1020	2.4	0.3	15.8	fcc-Pd	8.3
Pd(b)	$Pd(OAc)_2$	475	1.1	0.4	—	Amorphous	—
Pd(b)R	$Pd(OAc)_2$	530	0.9	0.74	—	fcc-Pd	1.6
Pd(b)OR	$Pd(OAc)_2$	642	0.9	0.9	—	fcc-Pd	5.6

[a] Determined from XRD. [b] Determined from HRTEM.

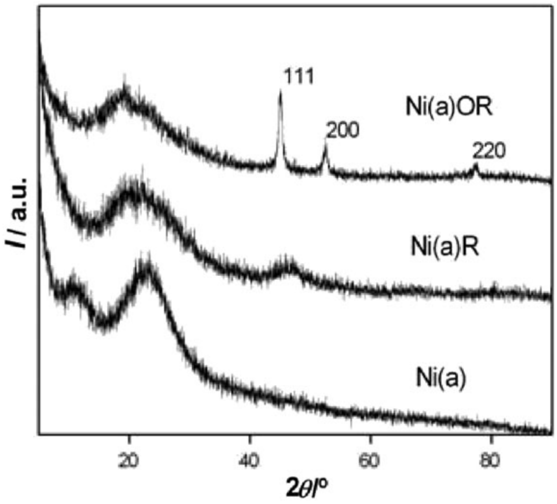


Fig. 3 Powder X-ray diffractograms of **Ni(a)**, **Ni(a)R** and **Ni(a)OR**.

in porosity and surface area. So, the temperature used to reduce the aerogels in the presence of H_2 promoted the partial removal of the organic groups with the concomitant creation of micropores.

The powder X-ray diffraction (XRD) patterns for the calcined–reduced aerogels showed the expected crystallinity of metallic fcc-Ni (Fig. 3) and fcc-Pd (Fig. 4) nanoparticles. We have determined the particle size by the XRD line broadening in case of sharp reflections (Table 1). As expected, small metallic nanoparticles were observed due to the high dispersion of the metal. For **Ni(*x*)R** aerogels, Ni(0) nanoparticles between 1.7 and 2.5 nm were observed. In the case of **Pd(*x*)R** the sizes of Pd(0) nanoparticles were even smaller (1.4–1.6 nm). Average particles size was larger for **M(a)OR** materials, the reason could be the longer thermal treatment which could result in an aggregation of the small particles, therefore favouring the particle growth. The influence of the various synthesis parameters on the particle size and the size distribution such as the nature of the complexing silane, the counter ion of the employed metal salt and the thermal process has already been investigated in detail.[5a,b,f,g,h]

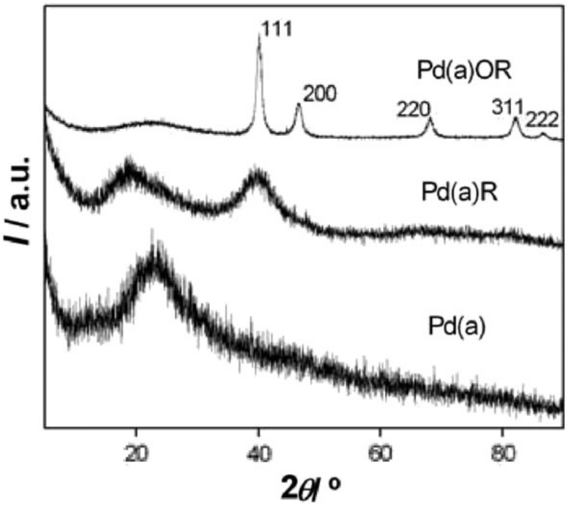


Fig. 4 Powder X-ray diffractograms of **Pd(a)**, **Pd(a)R** and **Pd(a)OR**.

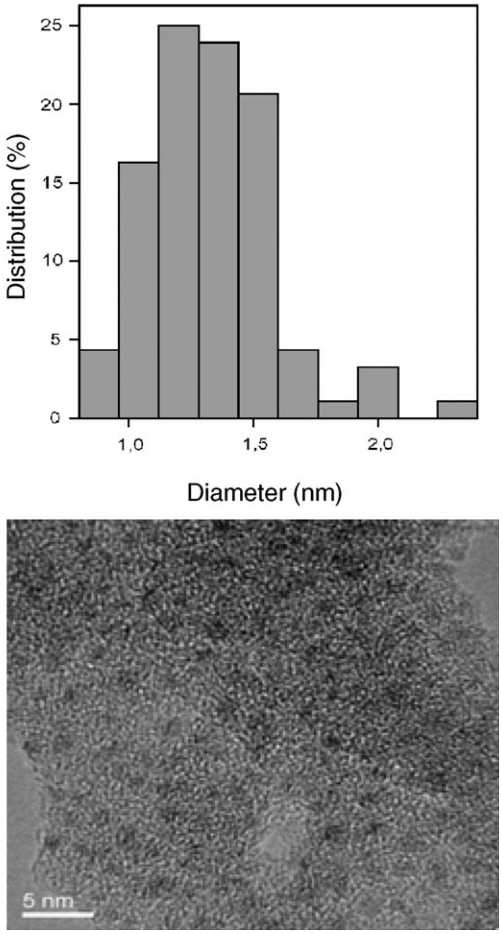
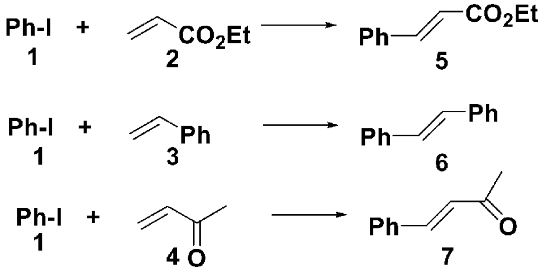


Fig. 5 Particle size distribution and HRTEM image of **Pd(a)**.

Transmission electron microscopy (TEM) of **Pd(a)** aerogels was carried out. It showed well defined spherical particles fairly homogeneously dispersed in the silica matrix (Fig. 5). The mean diameter of the nanoparticles determined by TEM was about 1.3 ± 0.3 nm. The electron diffraction patterns of this sample were obtained and the diffraction rings can be ascribed to the (111), (200), (220) and (311) crystallographic planes of the fcc-Pd. Therefore, the Pd is reduced in the supercritical conditions of the CO_2 and without the presence of any reduction step. This reduction process in supercritical conditions was observed previously for other Pd-doped aerogels dried in supercritical conditions of EtOH.[3]

The materials were tested as catalysts in Mizoroki–Heck reactions (Scheme 2, Table 2). For all the Mizoroki–Heck



Scheme 2 Mizoroki–Heck reactions tested.

Table 2 Results for Mizoroki–Heck reactions shown in Scheme 2

Catalyst	Olefin	Time/h	Product	Conversion[a] (%)
Pd(a)	**2**	24/35/45/40	**5**	97/90/85/98
Pd(a)R	**2**	8/11/13/20	**5**	99/93/90/83
Pd(a)OR	**2**	7/8/9/12	**5**	94/93/90/93
Pd(a)	**3**	3 days	**6**	82
Pd(a)R	**3**	10/25/23/48	**6**	74/65/56/79
Pd(a)OR	**3**	2 days	**6**	5
Pd(a)	**4**	3 days	**7**	98
Pd(a)R	**4**	2 days	**7**	99
Pd(a)OR	**4**	2 days	**7**	99

[a] Quantitative conversion by GLC chromatography.

reactions we used 2% molar palladium with respect to the limiting reagent and triethylamine as a base in refluxing CH_3CN. In general the best results were obtained for the **Pd(a)R** aerogel as catalyst. This material is very active for the reactions of iodobenzene with ethyl acrylate and styrene. In both cases we carried out the reaction three consecutive times with the same batch of catalyst without loss of activity. The analysis of the crude reaction mixture for the first reaction indicates a leaching of 3% for the **Pd(a)R**. In comparison with our previous results obtained with organic and carbon aerogels doped with Pd, we have improved the catalyst which is now more active and can be recovered and reused. As an example, the reaction of iodobenzene with ethyl acrylate is complete after 8 h using **Pd(a)R** as a promoter which can be reused three times, whereas our best results using a recoverable catalyst were obtained with Pd-carbon aerogel and a reaction time of 24 h.[3] A possible explanation could be the difference in the size of the metal particles. With the use of the ligand AEAPTS the metal is tethered to the silica matrix during sol–gel processing. This creates a good dispersion of the metal through the matrix and renders the aggregation of the Pd particles more difficult. This control over the particle size could be of importance in the case of using expensive metals.

Conclusions

Different Ni or Pd/silica aerogel nanocomposites were prepared. The use of the complexing silanes AEAPTS or TRIAMIN allows the metal to be tethered to the silica matrix during the preparation of the materials. Through TEM and XRD we can observe high metal dispersion and small particle sizes. The Pd aerogels were studied as catalysts in the Mizoroki–Heck reactions and they gave good results in the reaction between the iodobenzene and the ethyl acrylate or styrene. The advantages of using aerogels are the easy reaction work-up, and the easy recovery and reuse of the catalyst.

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References

1 For reviews on aerogels, see: (*a*) N. Hüsing and U. Schubert, *Angew. Chem., Int. Ed.*, 1998, **37**, 22; (*b*) A. C. Pierre and G. M. Panjonk, *Chem. Rev.*, 2002, **102**, 4243; (*c*) H. D. Gesser and P. C. Goswami, *Chem. Rev.*, 1989, **89**, 765.
2 S. Martínez, M. Meseguer, L. Casas, E. Rodriguez, E. Molins, M. Moreno-Mañas, A. Roig, R. M. Sebastián and A. Vallribera, *Tetrahedron*, 2003, **59**, 1553.
3 S. Martínez, A. Vallribera, C. L. Cotet, M. Popovici, L. Martín, A. Roig, M. Moreno-Mañas and E. Molins, *New J. Chem.*, 2005, **29**, 1342.
4 S. Martínez, L. Martín, E. Molins, M. Moreno-Mañas, A. Roig and A. Vallribera, *Monatsh. Chem.*, 2006, **137**, 627.
5 (*a*) B. Breitscheidel, J. Zieder and U. Schubert, *Chem. Mater.*, 1991, **3**, 559; (*b*) C. Lembacher and U. Schubert, *New J. Chem.*, 1998, 721; (*c*) G. Trimmel and U. Schubert, *J. Non-Cryst. Solids*, 2001, **296**, 188; (*d*) W. Rupp, N. Hüsing and U. Schubert, *J. Mater. Chem.*, 2002, **12**, 2594; (*e*) G. Trimmel, C. Lembacher, G. Kickelbick and U. Schubert, *New J. Chem.*, 2002, **26**, 759; (*f*) U. Schubert, S. Amberg-Schwab and B. Breitscheidel, *Chem. Mater.*, 1989, **1**, 576; (*g*) U. Shubert, B. Breitscheidel, H. Buhler, C. Egger and W. Urbaniak, *Mater. Res. Soc. Symp. Proc.*, 1992, **271**, 621; (*h*) W. Mörke, R. Lamber, U. Schubert and B. Breitscheidel, *Chem. Mater.*, 1996, **6**, 1659.
6 U. Schubert, *Adv. Eng. Mater.*, 2004, **6**, 173.
7 For a review on Mizoroki–Heck reaction catalyzed by supported palladium, see: A. Biffis, M. Zecca and M. Bassato, *J. Mol. Catal. A: Chem.*, 2001, **173**, 279.
8 (*a*) A. Papp, K. Miklós, P. Forgo and A. Molnár, *J. Mol. Catal. A: Chem.*, 2005, **229**, 107; (*b*) L. Li, L.-X. Zhang, J.-L. Shi, J.-N. Yan and J. Liang, *Appl. Catal., A*, 2005, **283**, 85.
9 H. Hagiwara, Y. Sugawara, T. Hoshi and T. Suzuki, *Chem. Commun.*, 2005, 2942.
10 For recent references, see: (*a*) G. Garcia and A. Leyva, *J. Mol. Catal. A: Chem.*, 2005, **230**, 97; (*b*) Q. Hu, J. Pang, N. Jiang, J. E. Hamsey and Y. Lu, *Microporous Mesoporous Mater.*, 2005, **81**, 149; (*c*) M. Gruber, S. Chouzier, K. Koehler and L. Djakovitch, *Appl. Catal., A*, 2004, **265**, 161; (*d*) K. Shimizu, S. Koizumi, T. Hatamachi, H. Yoshida, S. Komai and Y. Kitiyama, *J. Catal.*, 2004, **202**, 141; (*e*) A. Perosa, P. Tundo, M. Selva, S. Zinovyev and A. Testa, *Org. Biomol. Chem.*, 2004, **2**, 2249; (*f*) F. Zhao and M. Arai, *React. Kinet. Catal. Lett.*, 2004, **81**, 281; (*g*) N. Kim, M. S. Known, C. M. Park and J. Park, *Tetrahedron Lett.*, 2004, **45**, 7057.