Highly efficient and stable palladium nanocatalysts supported on an ionic liquid-modified xerogel†

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Incorporation of a phosphorylated ionic liquid as both a complexing and reducing agent for Pd(II) in a xerogel results in the formation of highly dispersed, uniformly sized Pd nanocatalysts, tightly supported on the surface of the silica and not embedded in the bulk of the xerogel.

The application of metal nanoparticles in catalysis has been an important frontier of research in recent years with numerous review articles published during the last decade in both heterogeneous[1] and homogeneous catalysis.[2] Heterogeneous catalysts are attractive for both laboratory and large scale processing. In fact, one of the challenging areas of research is heterogeneous catalysis with nanocatalysts supported on a solid surface. The possibility of the use of supported nanocatalysts in many areas of research, particularly in flow systems, offers not only the advantages of ease of automation, reproducibility, speed and safety,[3] but also the fact that no purification steps are usually needed and flow reactors can be used repeatedly, thus lowering the production costs.

Among different metal nanocatalysts, palladium nanoparticles have gained much reputation. This is because palladium is a versatile catalyst in modern organic synthesis and is widely used for a significant number of synthetic transformations[4] such as Mizoraki–Heck,[2b,5] Suzuki-cross coupling,[5b,c,6] Stille[7] and Sonogashira[7c] coupling reactions. However, its use is often complicated by issues surrounding the separation of the palladium and ligands from the desired product while reuse, ideally without loss of catalytic activity, becomes a major practical and economic issue with respect to large-scale applications. For this reason there has been much effort to immobilize palladium nanoparticles on suitable support surfaces. The most generally utilized methods for immobilization are physical adsorption in which palladium nanoparticles are supported on solid surfaces (e.g. silica, alumina or charcoal).[8] Over the past few years, a number of groups have immobilized a variety of palladium catalysts on a range of other insoluble supports, e.g. by coordination through resin-bound ligands or encapsulation in which palladium nanoparticles are trapped within a polymer backbone.[9] However, most of these supports are fragile and cannot withstand thermal activation or regeneration or their preparation is quite tedious. Also, the encapsulation of palladium nanoparticles in silicates or other solid substrates causes the active surface area of the nanoparticle to be very small which results in a decrease in their catalytic activity. This is the main disadvantage of the above procedures. Previous works on encapsulation of metal nanodispersions in sol–gel-derived silicates necessitate avoiding aggregation and precipitation of the metal salt or metallic particles in the organic sol–gel precursors and during the various stages of sol–gel polymerization, drying, and aging. Several general schemes were reported for the encapsulation of metallic nanoparticles in sol–gel matrices. Sequential reduction of metal salt and sol–gel processing in inverse micelle solutions[10] were used for the preparation of metal–silicate nanodispersions. However, the presence of gel precursors destabilizes the inverse micelles resulting in bigger particles and wider particle size distribution.[10]

In the search for an ideal support for Pd nanoparticles without such complications, we now report on the use of a phosphorylated ionic liquid (IL) modified xerogel which could be evenly coated on glass slides. As has been reported for other immidazolium ILs,[11] incorporation of this IL (I) in sol–gel films imparts considerable transparency, elasticity and reduced gel shrinkage to the silica matrix leading to the ease of evenly coating the sol–gel material on glass slides. It has been reported[12] that immidazolium based ILs form worm-like self assebmblies in sol–gel matrices through π–π stacking interactions of the neighboring imidazolium rings.[12]
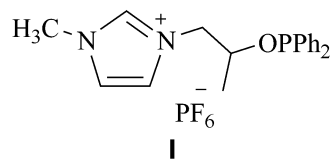
Herein we report the development of a novel method for the deposition of palladium nanoparticles on silica substrates. In this regard, we elucidated the effect of addition of a newly synthesized ionic liquid containing a phosphinite group (I)[13] attached to the silica matrix.

In contrast to the previous methods for immobilization of nanoparticles in silica matrices in which palladium nanoparticles were either added to the sol mixture during sol–gel preparation, or prepared during sol formation by calcinations

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and reduction processes, which result in dispersed nanoparticles *inside* a composite glass, here the xerogel containing self assemblies of the ionic liquid with a phosphinite group is first prepared and is then contacted with a solution of palladium acetate. The phosphinite group present in the IL acts both as a complexing and reducing agent for Pd(II). It has been established that a Pd(0) complex is spontaneously formed from reaction of Pd(II) and phosphine ligands by an irreversible intramolecular reduction of a Pd(II) complex by the phosphine.[14]

The important role of the presence of the ionic liquid containing a phosphinite group in a xerogel was further elucidated by substitution of the IL with 4-aminophenyl diphenyl phosphinite. In the latter case the formed xerogel did not have the ideal physical properties of a xerogel prepared with an IL and was not suitable for the formation of Pd nanoparticles.

The synthesis of phosphine stabilized palladium nanoparticles supported on silica was carried out using the following procedure. The xerogel was prepared by mixing tetraethoxysilane (TEOS) (1 ml), HCl (0.5 ml of 0.001M) and 0.1 g of IL powder. 1.5 ml of ethanol solution was added to this solution and the mixture was stirred for 30 min at room temperature. The solution was then allowed to gelate at room temperature for 24 h. The formed xerogel was deposited on a glass slide (activated with concentrated nitric acid) by immersion of the glass into the gel for 15 s and drying at room temperature under an ambient atmosphere for several days. Palladium nanoparticles were then supported on the xerogel by contacting (for 1 h), the glass slide with a solution of palladium acetate. Fig. 1 shows the occurrence of highly dispersed, uniformly sized Pd nanoparticles with an average size of 70 nm. The amount of Pd nanoparticles on the glass slide was determined by the ICP method and was found to be 286 ± 4 ng cm^{-2}.

Further support for the association of Pd nanoparticles with the surface of the glass slide was obtained by UV-Vis spectroscopy (Fig. 1S, ESI†) and AFM experiments (Fig. 2S, ESI†). The absence of the peak at 420 nm due to Pd(II) reveals complete conversion of Pd(II) to Pd(0). Also the AFM images show that the sol–IL functionalized surface is covered with tightly bound Pd nanoparticles.

The Pd nanoparticles thus obtained were found to be highly active, recyclable, and stable catalysts for wide applications. As some examples, the high catalytic effects of these nanocatalysts are presented in Suzuki and Heck coupling reactions in both organic solvents such as ethanol or DMF and also in
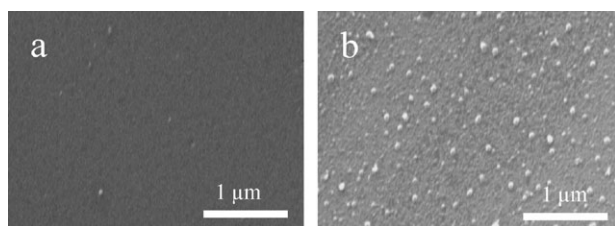

Fig. 1 SEM images of glass slides contacted with Pd(II) solution: (a) a glass slide covered with xerogel with no IL and (b) a glass slide covered with IL-modified xerogel.

Table 1 Suzuki and Heck reactions of aryl halides catalyzed by palladium nanoparticles

R=H, Me, OMe, COMe, NO$_2$

X=I, Br

Entry	Ar–X	Product	t/h	Yield^a (%)
1	Br-phenyl	biphenyl	9	95
2	MeO-phenyl-I	MeO-biphenyl	10	89
3	O$_2$N-phenyl-Br	O$_2$N-biphenyl	5	88
4	Br-phenyl-COMe	phenyl-phenyl-COMe	8	84
5	Br-phenyl	stilbene	15	95
6	MeO-phenyl-I	MeO-stilbene	15	88
7	O$_2$N-phenyl-Br	O$_2$N-stilbene	10	85

^{a} Isolated yield. Purity was confirmed by ^{1}H NMR.

water. Some representative reactions in ethanol are shown in Table 1. More interestingly, the Pd nanoparticles were found to be remarkably stable even under the high temperatures of reflux processes. The reusability of the Pd nanoparticles was tested for the Suzuki reaction between boromobenzene and phenyl boronic acid. A clear stability in activity was observed with the number of cycles up to 5 runs (RSD = 2.9%), (Table 1S, ESI†). The SEM images before and after the reactions show no considerable change in the morphology of the Pd nanoparticles. Thus, there is virtually no leaching of any Pd species.

The high catalytic effect of the Pd nanoparticles was also demonstrated on the chemiluminescent reaction of lumigen PS-atto and H$_2$O$_2$ which was chosen as a model system (Fig. 2). In this case the nanocatalyst can again be used several times without deterioration of its catalytic activity.

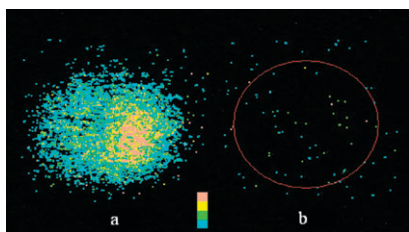The important feature of these highly dispersed supported Pd nanoparticles is that the nanoparticles are tightly

Fig. 2 Chemiluminescent intensity for the lumigen PS-atto–H$_2$O$_2$ system in the presence (a) and absence (b) of Pd nanoparticles.

supported on the *surface* of the silica and not embedded in the bulk of the xerogel. Thus, a larger active surface area of the catalyst is exposed on the xerogel. Due to this feature, mesoporous silica with nanoparticles can be successfully used as a catalyst in reactions where nanoparticles embedded in polymeric systems cannot be employed. The possibility of coating IL-modified xerogels, with high elasticity and low gel shrinkage, on a glass slide greatly facilitates handling and later separation of the catalyst from the reaction medium. Moreover, stabilization of nanoparticles in silica-based matrices provides a promising way to benefit from the advantages of nanocrystalline dispersions for optical and catalytic applications and still enjoy the convenience of solid handling.

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