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COMMUNICATION

Highly active Pd nanoparticles dispersed on amine functionalized layered double hydroxide for Suzuki coupling reaction†

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The synthesis of well dispersed palladium nanoparticles (1–5 nm) on diamine functionalized LDH is reported. The heterogeneous catalyst displayed unprecedented activity in Suzuki coupling reaction.

Palladium catalyzed Suzuki coupling is a fascinating reaction from a catalysis science perspective.[1] Pd nanoparticles as catalysts have led to a growing interest which in turn has resulted in an exponential growth in the number of nanoparticle synthesis procedures reported for this metal.[2] To date Pd nanoparticles have been prepared by methods like inverse micelle system,[3] reduction of palladium acetate,[4] electrochemical synthesis[5] or sonochemical reduction.[6] Noble metal nanoparticles have a characteristic large surface-to-volume ratio, and consequently large fractions of metal atoms are accessible to reactant molecules, which in turn greatly enhances the catalytic activity. However, small sized nanoparticle have the tendency to aggregate which makes the preparation procedure more laborious. Hence a major demand exists for the ability to produce well-defined monodispered Pd nanoparticles in the range of 1–4 nm. A key challenge in the application of these materials in catalysis is agglomeration of the nanoparticles, which can be overcome through surface functionalization/stabilization.[7]

The use of a heterogeneous catalyst in the liquid phase offers several advantages over homogeneous ones such as ease of recovery, and atom utility. Hydrotalcite of layered materials consist of cationic brucite layers and anionic compounds in the interlayer. The properties of the layered double hydroxide can be altered by incorporating different anionic complexes and enzymes through electrostatic interaction.[8] LDH supported nanopalladium catalyst for C–C coupling reactions has been reported by Choudary *et al.*[9] However, to the best of our knowledge reports on covalent attachment of various organic functionalities to the interlayer surface of LDH are rather scarce. But modification of the LDH surface with (3-aminopropyl) triethoxysilane by covalent attachment have been reported by Park *et al.*[10] by which unprecedented properties like a matrix and affinities for various organic and inorganic species other than conventional anionic guest can be obtained.

A heterogeneous system with the catalysts such as Pd/SiO_2,[11] Pd/C,[12] Pd complex grafted on SiO_2,[13] Pd complex intercalated in montmorillonite,[14] Pd/Al_2O_3 and Pd/resin,[15] Pd modified zeolite[16] is a desired option for commercial realization but affords poor to moderate conversion and selectivities in C–C coupling reactions.

Herein we describe a simple and efficient method for synthesis of monodispersed Pd nanoparticles on diamine functionalised LDH. The investigation of the reactivity of the resulting heterogeneous catalyst in Suzuki coupling would provide new information in fine chemical synthesis.

The layer double hydroxide containing Zn–Al with Zn:Al molar ratio 3 : 1 was prepared by the co-precipitation method at a constant pH.[17] ZnAl-LDH/SDS precursor was synthesized with 3 : 1 ratio of Zn(II) and Al(III) salts together with sodium dodecyl sulfate (SDS) as an intercalated anion. The synthesis was carried out by the co-precipitation method under a constant pH of ~7.[10] LDH/SDS and CTAB (cetyl trimethyl ammonium bromide) were dried at 80 °C overnight to maintain an anhydrous condition. 30 ml of methylene dichloride was added to 1.75 g of dried CTAB (0.16 M) under nitrogen atmosphere. 4.6 ml of N-[3-(trimethoxysilyl)-propyl] ethylenediamine (abbreviated as TPED) was added to the dried LDH precursor containing SDS. Then the CTAB solution containing methylene dichloride was added to the mixture of TPED and LDH/SDS. The whole mixture was allowed to react for two days at room temperature. Finally the product was filtered, washed thoroughly with methylene dichloride. The functionalized product was dried at room temperature and abbreviated as LDH/TPED.

0.2 g of $PdCl_2$ was dissolved in 10 ml of 2 M HCl solution of methanol. The whole Pd solution was transferred to a solution of 0.5 g functionalized LDH in 20 ml of methanol. The mixed solution was stirred for 2 h at room temperature and cooled overnight to 4 °C. The colored precipitate was filtered, washed several times with methanol and dried in air. The prepared Pd/LDH-complex (0.26 g) was reduced with $NaBH_4$ (0.25 g, 7 mmol) in tetrahydrofuran (10 ml) with constant stirring for 3 h at room temperature. Finally the product was separated by filtration and washed with tetrahydrofuran to give an air stable black colored powder. The final product was abbreviated as LDH-Pd^0 (Scheme 1).

The TEM images (Fig. 1) clearly revealed that most of the particles are uniformly dispersed; particle size and morphology are nearly identical. Some particles are in the range of 6–10 nm, but most had a size in the range of 2–5 nm. TEM image confirms the

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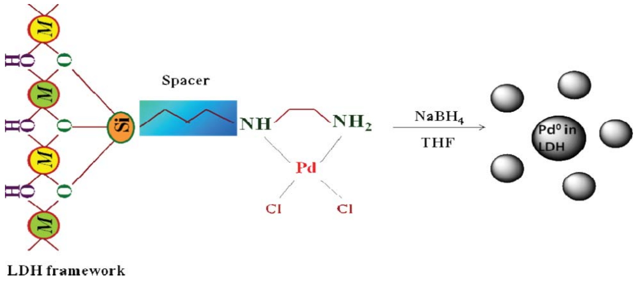
† Electronic Supplementary Information (ESI) available: XRD patterns, FTIR studies, mechanism responsible for covalent attachment, catalytic coupling reaction and catalytic reusability test up to four cycles. See DOI: 10.1039/c1dt10697j



Scheme 1 Schematic synthesis approach towards Pd^0 nanoparticles.

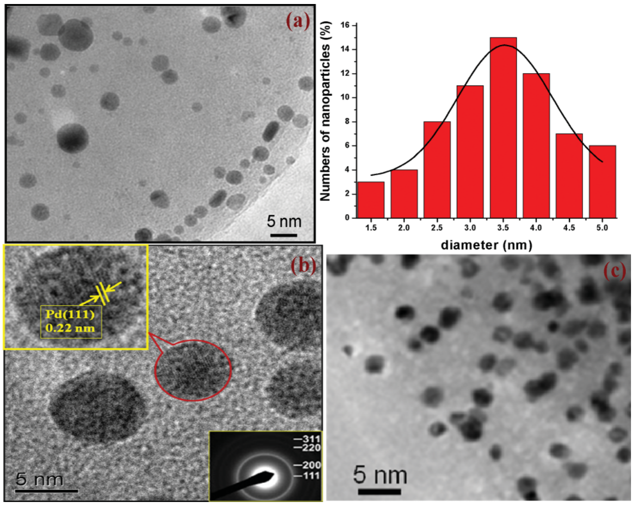


Fig. 1 (a) TEM image of Pd nanoparticles and histogram showing the size distribution for the Pd nanoparticles. (b) TEM image of Pd nanoparticles with electron diffraction pattern (inset, bottom right). (c) TEM image of the recycled catalyst.

highly crystalline nature of Pd particles. The interplanar spacing of 0.22 nm, obtained from the fringes of the lattice, agrees well with the (111) lattice spacing of face centered cubic (fcc) Pd. The electron diffraction pattern exhibits (Fig. 1(b), inserted) four diffuse rings that match well with the (111), (200), (220) and (311) reflections of the fcc metal.

The X-ray photoelectron spectrum (XPS) data was recorded (Fig. 2) in order to evaluate the exact oxidation state of palladium before and after reduction. The binding energy of Pd 3d$_{5/2}$ for the sample before reduction (Pd^{II}) was observed at 336.9 eV. After reduction 3d$_{5/2}$ and 3d$_{3/2}$ peaks appear at 335.4 and 340.7 eV respectively which are similar to the previously reported value for Pd^0.[18] This is an indication that Pd^{II} is reduced to Pd^0.

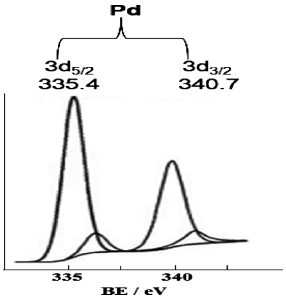


Fig. 2 X-ray photoelectron spectra of LDH-Pd(0).

^{29}Si CP MAS NMR spectra (Fig. 3) provide significant information about the degree of functionalization and to evaluate the nature of the M–O–Si bond around Si atom. Peaks in the T region (deconvolution data) are contributed by Si atoms of the triethoxy silane and are denoted by T^n (n = 0, 1, 2, 3), which are used to describe the extent of cross-linking depending on M–O–Si bond types. T^3 represents the formation of three Si–O–M bonds, which indicates complete cross-linking in the hybrid materials, while T^2 represents formation of two Si–O–M bonds bearing one uncoordinated Si-OEt group. High intensity of T^3 peak reveals the high degree of condensation of the original triethoxy silane with LDH.

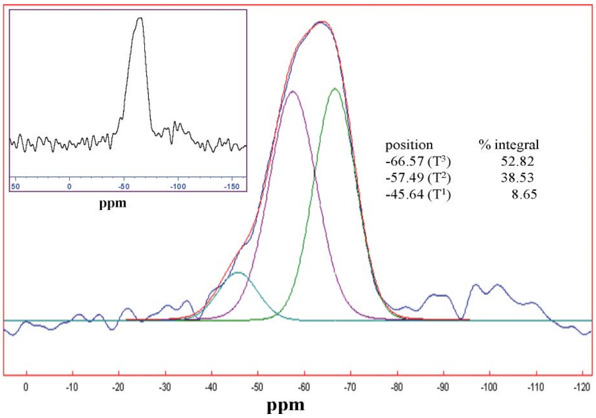
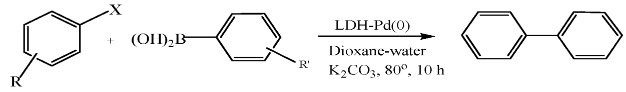


Fig. 3 ^{29}Si CP MAS NMR spectra of LDH/TPED.

We choose a basic support, Zn–Al LDH as the material of choice, not only to stabilize the nanopalladium particles but also to provide adequate electron density to anchored Pd^0 species to facilitate the oxidative addition of halobenzene to Pd^0. It is well

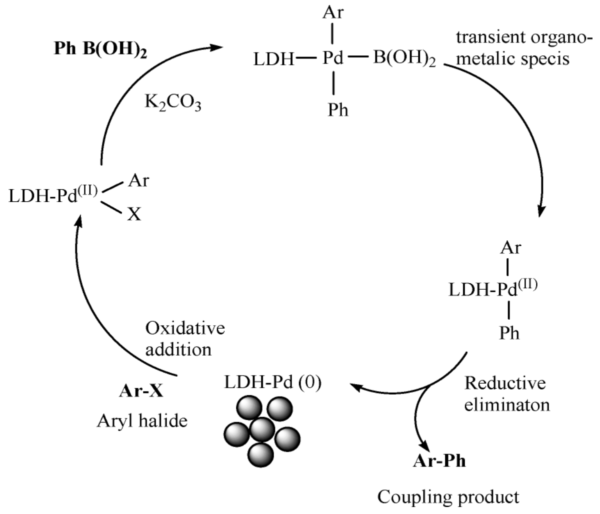
Table 1 Coupling of chloroarenes with arylboronic acid in the presence of LDH-Pd(0)



Entry	R, X	R′	Yield (%)
1	H, Br	H	94
2	4-Me, Br	H	86
3	4-MeO, Br	H	75
4	4-NO$_2$, Br	H	91
5	H, Br	4-MeO	65
6	H, Br	4-Me	76
7	H, I	H	96
8	4-Me, I	H	83
9	4-MeO, I	H	81
10	4-NO$_2$, I	H	90
11	H, I	4-MeO	72
12	H, I	4-Me	78
13	H, Cl	H	88
14	4-Me, Cl	H	77
15	4-MeO, Cl	H	70
16	4-NO$_2$, Cl	H	82
17	H, Cl	4-MeO	64
18	H, Cl	4-Me	71

Reaction conditions: Haloarene (1 mmol), aryl boronic acid (1.5 mmol), potassium carbonate (3 mmol), Pd(0) catalyst (0.03 g), 1,4-dioxane–water(5 : 1) = 10 ml, T = 80 °C, time = 10 h.

known that the activation of the C–Cl bond is much more difficult than the C–Br and C–I bonds and in general requires harsher conditions in a heterogeneous catalytic system. But in the present study the reaction results are quite impressive for aryl chlorides (Table 1). The LDH supported Pd^0 catalyst is potent enough to activate the C–Cl bond to produce biaryl compounds showing great potential for practical applications. The possible mechanistic pathway is depicted in Scheme 2. The reaction is believed to pass through the oxidative addition of aryl halides to Pd^0 followed by the formation of transient organo-metallic species reaction with boronic acid.[19]



Scheme 2 Plausible mechanistic pathway for Suzuki coupling.

Generally, mineral bases are such as alkali metal carbonates or K_3PO_4 are used as bases in Suzuki coupling. The use of water either as a solvent or additive [20] help with the solvation of these organic-insoluble materials. Also, as organoboron compounds are quite often stable to protolytic decomposition by water.[21] Cammidge and co-workers have reported heterogeneous Pd phosphine catalysts and used these in Suzuki coupling in a DME:water (3 : 1) solvent mixture.[22] Low yields are obtained with nonpolar solvents such as toluene and o-xylene, while polar solvents such as tetrahydrofuran, 1,4-dioxane and 1,4-dioxane–water (5 : 1) gave good yields.

Notably, it was reported that the reduced Pd^0 species were more easily leached into the solution than Pd^{II} species.[23] Hence the use of heterogeneous catalyst, free from Pd leaching and agglomeration, is highly desirable for achieving high activity and catalyst reusability. In this context, the catalyst was removed from the solution after approximately 50% conversion at the reaction temperature. The isolated solution did not exhibit any further reactivity under similar reaction conditions. These studies indicate that the loss of the palladium active site is negligible, which could account for the preservation of catalytic activity. The used catalyst was examined by TEM (Fig. 1(c)) after the completion of the reaction and the result clearly showed that Pd particles remains homogeneously dispersed on the support, without any appreciable change in size and morphology. It is envisaged that palladium nanoparticles stabilized by TPED could potentially be exploited more extensively in the field of catalysis in contrast to bulky stabilizers such as dendrimers, polymers and alkanethiols.

In conclusion, we have shown that functionalization provides a better control of the loading of palladium and a relatively uniform distribution of nanoparticles in the layered material. Most importantly, the catalyst was reusable without Pd leaching and agglomeration which is an important step towards a simple system with the potential for commercial exploitation of heterogeneous catalysts in water-mediated C–C coupling reactions.

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