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One-Step Co-condensation Method for Synthesis of Well-Defined Functionalized Mesoporous SBA-15 Using Trimethylsilylanes as Organosilane Sources

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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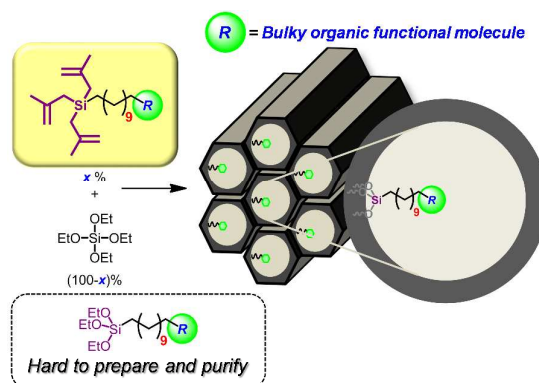
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New method for preparation of well-defined functionalized mesoporous SBA-15 has been developed by one-step co-condensation method using trimethylsilylanes as organosilane sources. This new method enables incorporation of various bulky organic functional groups with long alkyl chain tether to the mesoporous silica network.

Fabrication of high performance, organo-functionalized mesoporous silica has received considerable attention owing to the high recyclabilities and enhanced stabilities of these materials.¹⁻⁴ Among many approaches devised for this purpose, co-condensation methods employing alkoxysilanes have been most often used to introduce organic functional groups into silica networks. Advantageous features of the functionalized silicas generated in this manner include high loading efficiencies and homogeneous surface coverages.⁵ However, alkoxysilanes, commonly used in this technique, are difficult to functionalize and purify.¹⁻⁶ As a consequence, applicable substrates employed in this approach are limited to distillable short chain alkoxysilanes containing a small range of functionalities.²⁻⁴ And often inefficient, multistep functional group transformations must be performed on the mesoporous materials to generate desired functional mesoporous silica materials. Another formidable challenge when alkoxysilane-based protocols are utilized is the difficulty in preparing materials that contain functional groups attached to the silica surface through long tethers. This is an important feature because long tether enables ideal interactions to take place between the immobilized catalytic moieties with substrates, a requirement for high catalytic performance.⁷

In earlier studies, we developed an efficient grafting method, which utilizes methylsilylanes as alkoxysilane surrogates, for installation of organic functional group on silica surface.^{7b,8} Considering their unique properties, including high stability in functional group transformation reactions and

purification processes, and their intrinsic lability under acidic conditions, trimethylsilylanes (**1**) serve as ideal precursors of functionalized mesoporous silicas (SBA-15s).^{9,10} In the studies described below, we developed a new co-condensation method using trimethylsilylanes containing bulky organic functional groups linked through long tethers (Figure 1).¹² A notable feature of this approach is its ability to produce high performance functionalized SBA-15s through a direct, one-pot co-condensation protocol. Specifically, we observed that reaction of properly structured trimethylsilylanes with TEOS under acidic conditions generates long alkyl chain-tethered functionalized mesoporous silicas that are otherwise difficult to prepare. Finally, in this effort we employed the functionalized, organic and organometallic group-impregnated SBA-15s as recyclable catalysts to promote highly efficient reactions.



Notable Features

- Pure undistillable trimethylsilylane precursor applied
- Readily accessible to functional SBA-15
- Long alkyl chain tether for remarkable activity of functional group

Figure 1. Advantage of one-step synthesis of functionalized SBA-15 using functional organotrimethylsilylanes with an undecyl tether.

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Electronic Supplementary Information (ESI) available: [Experimental details and characterization of new materials]. See DOI: 10.1039/x0xx00000x

The first phase of this investigation was designed to demonstrate the practical utility of a new, one step method for synthesizing functionalized SBA-15s. As a model

trimethylsilyl silane substrate for this process, we selected 4-(pyren-1-yl)-1-(11-(tris(2-methylallyl)silyl)undecyl)-1H-1,2,3-triazole (**1a**), which contains pyrenyl groups tethered through a long alkyl chain to the methylsilyl moiety. We reasoned that successful incorporation of pyrenyl groups on the silica surface would be easily demonstrated by using fluorescence techniques. The desired silane **1a** was prepared by using Cu(I)-promoted [3+2]-cycloaddition reaction¹¹ of 1-ethynylpyrene with 11-azidoundecyltrimethylsilyl silane, and purified by using silica-gel chromatography. The modified procedure described by Gupta and coworker was applied in this co-condensation method.^{5c} The reaction of TEOS (Tetraethyl orthosilicate) with **1a** (TEOS/**1a**) in the presence of aqueous HCl and P123 followed by solvent extraction gave the pyrene functionalized SBA-15, **Pyr@Si**. Under the reaction conditions, the trimethylsilyl silane moiety is completely consumed, as determined by using ¹H NMR spectroscopy.¹² The one-pot co-condensation process was carried out using different ratios (99/1, 95/5, 90/10 and 85/15) of TEOS and **1a** (Figure 2a). The loading of pyrene triazolyl groups on the surfaces of the resulting materials, determined by using elemental analysis, was found to increase linearly as the amount of **1a** used in the reaction increases up to 15% (0.12 mmol g⁻¹ for 1% **1a**; 0.40 mmol g⁻¹ for 5% **1a**; 0.77 mmol g⁻¹ for 10% **1a**; 1.0 mmol g⁻¹ for 15% **1a**, Figure 2b).

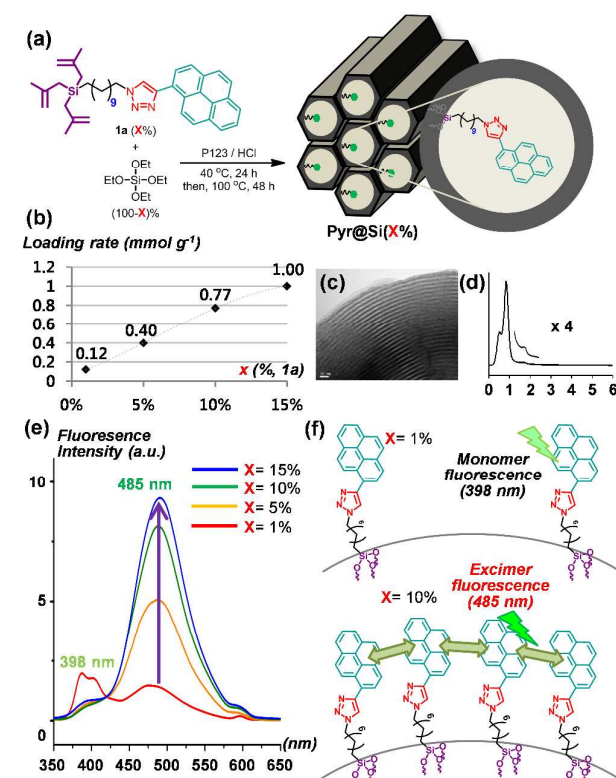


Figure 2. (a) Pyrenetriazolyl functionalized SBA-15s (**Pyr@Si**s) prepared using different ratios of TEOS and **1a** (99/1, 95/5, 90/10, and 85/15) in one-step co-condensation method. (b) Loading of pyrene triazolyl groups in each **Pyr@Si**. (c) TEM image of **Pyr@Si(15%)**, (d) SAXS of **Pyr@Si(15%)**, (e) Fluorescence spectra of **Pyr@Si(1%)**, **Pyr@Si(5%)**, **Pyr@Si(10%)** and **Pyr@Si(15%)** (normalized at 414 nm). (f) Illustrational rationale for the excimer peak of 485 nm.

Thus, the amount of pyrenyl groups on the functionalized mesoporous SBA-15 can be controlled by simply regulating the ratio of TEOS and **1a**. TEM (Figure 2c) and SAXS (Figure 2d) of the **Pyr@Si(15%)** gave data that correspond directly to those of the original SBA-15.^{5b} The ¹³C CP-MAS solid-state NMR spectrum of **Pyr@Si(15%)** clearly displays peaks that are representative of the pyrene-triazolylundecyl group (see ESI, Figure S2).

We also determined the fluorescence properties of the **Pyr@Si**s containing different pyrene loading levels (Figure 2e). The emission spectrum of the low pyrene group-embedded **Pyr@Si(1%)** contains maxima at 398 nm with a weak peak at 485 nm. In contrast, **Pyr@Si**s containing greater than 5% loading have fluorescence spectra in which the band at 485 nm becomes more intense relative to the 398 nm band in a manner that is dependent on the %-loading. The observations are consistent with assignment of the maximum at 485 nm to emission from excimers which become more dominant as the surface is more populated by pyrene fluorophores (Figure 2f). This phenomenon was also observed earlier by Stack et al.^{5a,5b} Therefore, the results of this analysis show clearly that the extent of pyrene group loading on the surface of mesoporous silica can be readily determined by using fluorescence spectroscopy.

The one-step, co-condensation reaction was performed using 4-(dimethylamino)azobenzene-4'-sulfonyl (dabsyl) group containing trimethylsilyl silane **1b** (Figure 3a). Reactions utilizing various ratios of TEOS and **1b** lead to formation of the dabsyl group linked SBA-15s with loading levels in the range of 0.11–0.78 mmol/g. The loading amount on the SBA-15 was readily determined by using elemental analysis and measuring the intensity of the red color associated with the dabsyl group (Figure 3b-c). It is noteworthy that analysis of TEM images show that the mesoporous structures of **Dabsyl@Si** are retained up to 15% loading of dabsyl groups (see ESI).

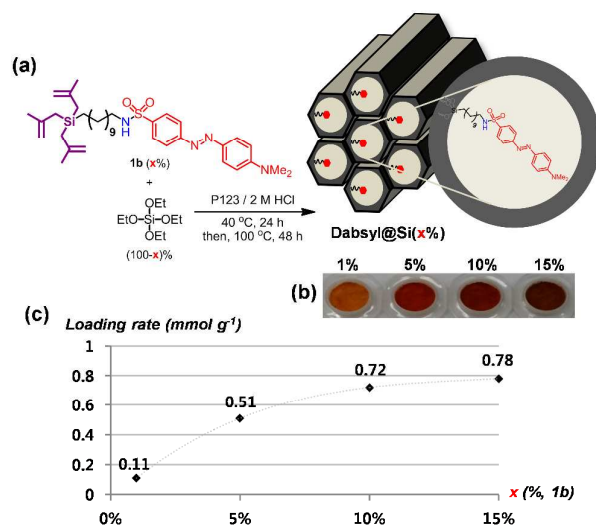


Figure 3. (a) Preparation of **Dabsyl@Si**s from using different ratios of TEOS and **1b** (99/1, 95/5, 90/10, 85/15) utilizing the co-condensation method. (b) Intensity change of red color and (c) Loading rate of Dabsyl group in **Dabsyl@Si(1%)**, **Dabsyl@Si(5%)**, **Dabsyl@Si(10%)** and **Dabsyl@Si(15%)**.

The SBA-15s, prepared by using the approach described above, contain functional groups that are tethered to the silica surface through long alkyl chains. Consequently, it is anticipated that these functionalized mesoporous silicas will display much higher catalytic activities than conventional functionalized SBA-15 with short tethers owing to the fact that the pendant functional groups can better interact with substrates.⁷ To evaluate this hypothesis, a study was conducted to probe the use of an amine containing catalyst of this type to promote a Knoevenagel reaction.

For this purpose, we prepared primary amine-functionalized SBA-15s from the corresponding azide-functionalized silicas, **Pr-N₃@Si** and **Und-N₃@Si**, which were synthesized by using one-pot co-condensation reactions of the respective 3-azidopropyltrimethylsilyl silane (**1c**) and 11-azidoundecyltrimethylsilyl silane (**1d**) with TEOS (TEOS/**1c**, TEOS/**1d** = 90/10) (Figure 4a). The amine functionalized SBA-15s, **Pr-NH₂@Si** and **Und-NH₂@Si**, were then generated from the corresponding azides through Staudinger reactions,¹³ involving treatment with a mixture of PPh₃ and water. The success of these processes was demonstrated by analysis of the IR spectra of the products, which showed that peaks at 2110 cm⁻¹ corresponding to the azide moiety were absent (See ESI, Figure S3).

The amine-functionalized silicas, **Pr-NH₂@Si** and **Und-NH₂@Si**, were tested as catalysts for Knoevenagel reaction of malononitrile (**2**) with benzaldehyde (**3**) (Figure 4b).¹⁴ Reaction between **2** and **3**, carried out using **Und-NH₂@Si** as catalyst at ambient temperature for 2 h resulted in the formation of 2-benzylidenemalononitrile (**4**) in a quantitative yield. Under identical conditions, the condensation reaction promoted by **Pr-NH₂@Si** required 8 h to complete (Figure 4c). The results show that **Und-NH₂@Si**, in which the amine group is tethered to the silica surface by a longer alkyl chain, is a superior catalyst for the Knoevenagel reaction.

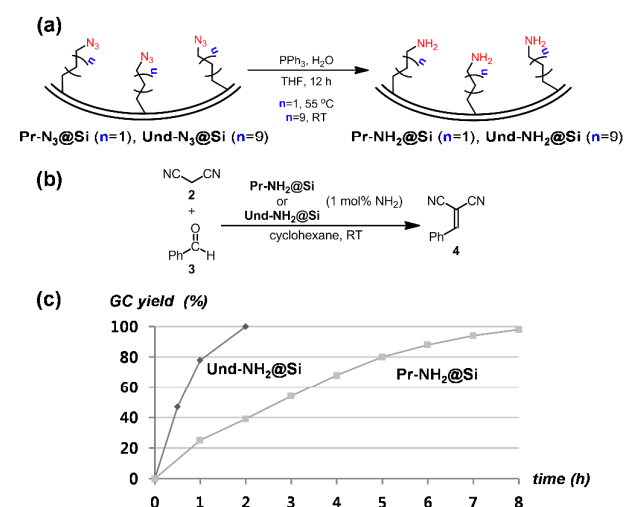


Figure 4. (a) Synthesis of amine functionalized SBA-15s (**Pr-NH₂@Si** and **Und-NH₂@Si**) through Staudinger reaction of **Pr-N₃@Si** and **Und-N₃@Si** with PPh₃ and H₂O. (b) Knoevenagel reactions of malononitrile and benzaldehyde using **Pr-NH₂@Si** and **Und-NH₂@Si** as catalysts. (c) GC yield (%) of products **4** versus reaction time.

This finding suggests that interactions between the catalytic groups in **Und-NH₂@Si** and substrates are superior to those occurring with **Pr-NH₂@Si**.

The new approach was also employed to prepare a silica based catalytic system containing a supported transition metal.¹⁵ Because imidazolium group are readily transformed into 4-imidazoline (NHC) ligands for Pd when treated with Pd(OAc)₂,¹⁶ imidazolium group containing trimethylsilyl silane **1e** was selected as the reagent for preparation of the modified mesoporous silica. Trimethylsilyl silane derivative **1e** was prepared by reaction of 11-chloroundecyltrimethylsilyl silane with 1-mesityl-1H-imidazole at 120 °C for 24 h.¹⁷ Co-condensation of TEOS with **1e** (TEOS/**1e** = 90/10) then generated the imidazolium-bound SBA-15, **Imid@Si** (1.13 mmol/g loading, Figure 5a). A TEM image of the modified silica shows that it contains a uniform distribution of mesopores (Figure 5b, pore size: 3.1 nm), and inspection of its ¹³C CP-MAS NMR spectrum shows that it contains surface imidazolium groups (see ESI, Figure S4). In addition, solid state ²⁹Si NMR spectra of **Imid@Si** shows Q₃ (single silanol), Q₄ (silicate) and T₃[R(SiO)₃Si] signals, which are consistent with previously reported data of functionalized SBA-15 prepared by the classical alkoxy silane protocol (see Figure S5 in ESI).^{5c}

The Pd-NHC complex-tethered SBA-15, **Pd-NHC@Si**, was prepared by first blocking residual surface silanol groups in **Imid@Si** by treatment with trimethylchlorosilane (TMCS) and then carrying out reaction with Pd(OAc)₂ in toluene at reflux.¹⁸ The loading of Pd in the resulting **Pd-NHC@Si** was determined to be 2.9% by using ICP-MS. In addition, the existence of the transition metal in its Pd²⁺ state was demonstrated by analysis of the XPS spectrum (see ESI), which contains a Pd(3d) peak at 337 eV that is identical to previously reported value for the Pd²⁺ state.¹⁸

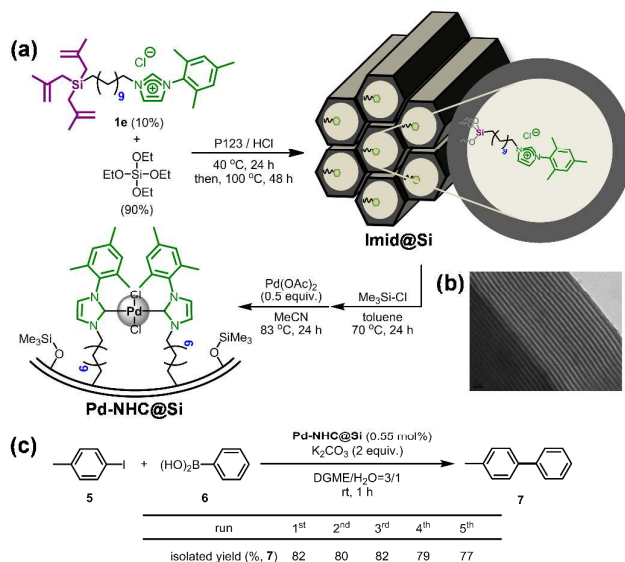


Figure 5. (a) One-step synthesis of imidazolium salt functionalized SBA-15 (**Imid@Si**) and preparation of **Pd-NHC@Si**. (b) TEM image of **Imid@Si**. (c) Suzuki reaction using **Pd-NHC@Si** as a catalyst and isolated yields of recycled catalytic reactions.

The catalytic activity of **Pd-NHC@Si** was demonstrated by its use to promote a Suzuki coupling reaction of 4-iodotoluene (**5**) with phenylboronic acid (**6**). Reaction of **5** with **6** in the presence of **Pd-NHC@Si** (0.55 mol%) at room temperature gave 4-methyl-1,1'-biphenyl (**7**) in 82% isolated yield (Figure 5c).¹⁹ The insoluble catalyst **Pd-NHC@Si**, recovered from the reaction mixture by using centrifugation, was reused for a second Suzuki cross coupling reaction between **5** and **6**, which produced **7** in an 80% yield.²⁰ The results of experiments in which recovered **Pd-NHC@Si** was employed repeatedly showed that its catalytic efficiency is retained even after five cycles and that the transition metal remains in the Pd²⁺ state.

In the study described above, we have devised a new method for preparation of functionalized mesoporous silicas that takes advantage of the characteristic properties of methallylsilanes, notably their high stabilities during functional group transformations and purification, and their labilities under acidic conditions. These unique properties have been used to develop a method for one-step synthesis of high-performance, functionalized mesoporous silicas from appropriately modified organo-trimethallylsilanes that contain functional groups tethered through long alkyl chains. Employing this method, a variety of bulky functional groups such as a fluorophore, chromophore, and even ionic imidazolium moiety for recycling transition metal catalyst can be incorporated into mesoporous silica network with loading extents of up to 15% of the organosilane (ca. 1.0 mmol/g). The new method developed in this effort overcomes the limitations of the conventional alkoxy silane approach and the accompanying requirement for inefficient multistep, solid-phase transformations.

This work was supported by a grant from the National Research Foundation of Korea (NRF) (Grant 2011-0016830).

Notes and references

- For reviews, (a) K. B. Yoon, *Acc. Chem. Res.*, 2007, **40**, 29; (b) F. Hoffmann, M. Cornelius, J. Morell and M. Fröba, *Angew. Chem. Int. Ed.*, 2006, **45**, 3216; (c) A. B. Descalzo, R. Martínez-Mañez, F. Sancenó, K. Hoffmann and K. Rurack, *Angew. Chem. Int. Ed.*, 2006, **45**, 5924; (d) A. Schlossbauer, D. Schaffert, J. Kecht, E. Wagner and T. Bein, *J. Am. Chem. Soc.*, 2008, **130**, 12558.
- C. Sanchez, B. Julian, P. Belleville and M. Popall, *J. Mater. Chem.*, 2005, **15**, 3559.
- G. F. Hays, A. D. H. Clague, R. Huis and G. Van Der Velden, *Appl. Surf. Sci.*, 1982, **10**, 247.
- A. Sayari and S. Hamoudi, *Chem. Mater.*, 2001, **13**, 3151.
- For selected recent examples, see: (a) J. Nakazawa and T. D. P. Stack, *J. Am. Chem. Soc.*, 2008, **130**, 14360; (b) J. Nakazawa, B. J. Smith and T. D. P. Stack, *J. Am. Chem. Soc.*, 2012, **134**, 2750; (c) B. Malvi, B. R. Sarkar, D. Pati, R. Mathew, T. G. Ajithkumar and S. S. Gupta, *J. Mater. Chem.*, 2009, **19**, 1409; (d) S. Huh, J. W. Wiench, J.-C. Yoo, M. Pruski and V. S.-Y. Lin, *Chem. Mater.*, 2003, **15**, 4247.
- (a) C. M. Crudden, M. Sateesh and R. Lewis, *J. Am. Chem. Soc.*, 2005, **127**, 10045; (b) G. J. A. A. Soler-Illia and P. Innocenzi, *Chem. Eur. J.*, 2006, **12**, 4478; (c) A. Corma and H. Garcia, *Adv. Synth. Catal.*, 2006, **348**, 1391; (d) E. J. Acosta, C. S. Carr, E. E. Simanek and D. F. Shantz, *Adv. Mater.*, 2004, **16**, 985; (e) Y. Fujimoto, A. Shimojima and K. Kuroda, *Chem. Mater.*, 2003, **15**, 4768; (f) P. Judeinstein and C. Sanchez, *J. Mater. Chem.*, 1996, **6**, 511.
- (a) S. Park and I. Shin, *Angew. Chem. Int. Ed.*, 2002, **41**, 3180; (b) U.-Y. Jung, J.-W. Park, E.-H. Han, S.-G. Kang, S. Lee and C.-H. Jun, *Chem. Asian J.*, 2011, **6**, 638.
- (a) Y.-R. Yeon, Y. J. Park, J.-S. Lee, J.-W. Park, S.-G. Kang and C.-H. Jun, *Angew. Chem. Int. Ed.*, 2008, **47**, 109; (b) J.-W. Park, Y. J. Park and C.-H. Jun, *Chem. Commun.*, 2011, **47**, 4860; (c) D. H. Lee, E.-A. Jo, J.-W. Park and C.-H. Jun, *Tetrahedron Lett.*, 2010, **51**, 160; (d) S. Park, J. Pai, E.-H. Han, C.-H. Jun and I. Shin, *Bioconjugate Chem.*, 2010, **21**, 1246.
- For immobilization of organic functional group onto silica using allylsilane, see: (a) T. Shimada, K. Aoki, Y. Shinoda, T. Nakamura, N. Tokunaga, S. Inagaki and T. Hayashi, *J. Am. Chem. Soc.*, 2003, **125**, 4688; (b) K. Aoki, T. Shimada and T. Hayashi, *Tetrahedron: Asymmetry*, 2004, **15**, 1771; (c) Y. Maegawa, T. Nagano, T. Yabuno, H. Nakagawa and T. Shimada, *Tetrahedron*, 2007, **63**, 11467; (d) Y. Wang, S. Hu and W. J. Brittain, *Macromolecules*, 2006, **39**, 5675.
- For examples describing the synthesis of periodic mesoporous organosilica using bis(allylsilane) derivatives, see: M. P. Kapoor, S. Inagaki, S. Ikeda, K. Kakiuchi, M. Suda and T. Shimada, *J. Am. Chem. Soc.*, 2005, **127**, 8174.
- (a) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem. Int. Ed.*, 2001, **40**, 2004; (b) Q. Wang, T. R. Chan, R. Hilgraf, V. V. Fokin, K. B. Sharpless and M. G. Finn, *J. Am. Chem. Soc.*, 2003, **125**, 3192.
- The trimethallylsilyl group was determined to be labile under acidic SBA-15 synthetic condition. See supporting information for details. For a related report describing solvent effect on sol-gel polymerization of allylsilane, see: Y. Maegawa, N. Mizoshita, T. Tani, T. Shimada and S. Inagaki, *J. Mater. Chem.*, 2011, **21**, 14020.
- (a) Y. G. Gololobov, I. N. Zhmurova and L. F. Kasukhin, *Tetrahedron*, 1981, **37**, 437; (b) M. Vaultier, N. Knouzi and R. Carrie, *Tetrahedron Lett.*, 1983, **24**, 763.
- M. N. Parvin, H. Jin, M. B. Ansari, S.-M. Oh and S.-E. Park, *Appl. Catal. A-Gen.*, 2012, **413**, 205.
- For recent examples about studies on metal-NHC complexes immobilized onto mesoporous silica, see: (a) M. K. Samantaray, J. Alauzun, D. Gajan, S. Kavitate, A. Mehdi, L. Veyre, M. Lelli, A. Lesage, L. Emsley, C. Copéret and C. Thieuleux, *J. Am. Chem. Soc.*, 2013, **135**, 3193; (b) M. P. Conley, R. M. Drost, M. Baffert, D. Gajan, C. Elsevier, W. T. Franks, H. Oschkinat, L. Veyre, A. Zagdoun, A. Rossini, M. Lelli, A. Lesage, G. Casano, O. Ouari, P. Tordo, L. Emsley, C. Copéret and C. Thieuleux, *Chem. Eur. J.*, 2013, **19**, 12234; (c) M. P. Conley, C. Copéret and C. Thieuleux, *ACS Catal.*, 2014, **4**, 1458.
- N. Marion, S. Diez-Gonzalez and S. P. Nolan, *Angew. Chem. Int. Ed.*, 2007, **46**, 2988.
- M. G. Gardiner, W. A. Herrmann, C.-P. Reisinger, J. Schwarz and M. Spiegler, *J. Organomet. Chem.*, 1999, **572**, 239.
- G. Liu, M. Hou, T. Wu, T. Jiang, H. Fan, G. Yang and B. Han, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2062.
- E. Tyrrell, L. Whiteman and N. Williams, *J. Organomet. Chem.*, 2011, **696**, 3465.
- This result implies that Pd²⁺ is coordinated to NHC ligand on silica surface. For comparison, when the Pd-adsorbed silica with no NHC ligand, prepared by treatment of SBA-15 with TMCS and Pd(OAc)₂, was applied for recycling experiment, no reaction occurred after 2nd recycle due to complete leaching of Pd²⁺ (only 63% yield of Suzuki coupling product was obtained in the first run).