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Catalysis with chemically modified mesoporous silicas: Stability of the mesostructure under Suzuki–Miyaura reaction conditions

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The use of functionalized mesoporous silicas such as SBA-15 and MCM-41 as supports for Pd catalysis has become increasingly common, notably in important reactions such as the Suzuki–Miyaura reaction. However the analysis of the structural consequences of exposure to these harsh reaction conditions is not nearly as common. We report herein a study of the effect of the Suzuki–Miyaura reaction conditions on the mesoporous material, and on the catalytic activity of the resulting material. Although it has been determined that aqueous base is highly detrimental to the structure of the material, the boric acid produced during the actual coupling reaction has a significant protective effect on the material. This protective effect can be mimicked by the addition of exogenous boric acid to the reaction medium. The use of aluminum-doped material provides an additional protective effect that is not dependent on the presence of boric acid. Finally, we demonstrate conclusively that access to the pores is essential for catalysis, since loss of mesoporosity is coincident with loss of catalytic activity.

1. Introduction

Despite the remarkable importance of metal-catalyzed transformations in the synthesis of fine chemicals, pharmaceuticals, and commodity chemicals, contamination of the organic products with metals remains a serious challenge [1]. The Suzuki–Miyaura reaction (Scheme 1) [2,3] stands out among the currently available coupling reactions for the synthesis of pharmaceutical compounds as the most commonly employed reaction in the pharmaceutical industry for the formation of carbon–carbon bonds [4]. However, considering the strict guidelines placed on Pd levels in products destined for human consumption [1], there is a great need for methods to prevent Pd incorporation into the organic products of this important reaction. These methods can be broadly divided into scavenging and preventative approaches, the latter being dominated by the use of leach-resistant heterogeneous catalysts.

Our group and others [5–9] have shown that it is possible to use mercaptopropyl trialkoxysilane-modified materials both as scavengers for soluble Pd and as recoverable catalysts that leach low amounts of Pd into solution. The support most commonly employed for the thiol-ligated Pd is SBA-15 [10–12], a mesoporous silica material with high porosity and, compared to other mesoporous materials, relatively good stability. However, for extended use of these materials in the Suzuki–Miyaura reaction, their stability to the reaction conditions, particularly hot aqueous base, needs to be assessed. Although the thermal and hydrothermal stability of mesoporous materials has been exhaustively studied [13–17], their stability to other more forcing reaction conditions such as those employed herein, has received little or no attention.

Thus we report herein the effect of the Suzuki–Miyaura reaction conditions on supported heterogeneous catalysts derived from a variety of materials, and the effect of material collapse on the resulting catalytic activity. MCM-41, calcined SBA-15, Al-stabilized SBA-15, and various other materials have been subjected to typical Suzuki–Miyaura reaction conditions, and the resulting effects on the materials properties and catalytic activities are described. We demonstrate the protective effects of elements such as aluminum and boron on the order of the material under these harsh reaction conditions. We also demonstrate conclusively that access to the interior pores of the material is essential for catalytic activity.

2. Materials and methods

2.1. Chemicals

Pluronic P123 ($EO_{20}PO_{70}EO_{20}$), tetraethyl orthosilicate (TEOS), sodium aluminate ($NaAlO_2$), sodium chloride, decane, dimethoxybenzene (DMB) potassium carbonate, and pinacol were obtained from Aldrich and were used without further purification. Bromoacetophenone (BrPhAc, Aldrich) was recrystallized from ethanol. Phenyl boronic acid and $Pd(OAc)_2$ were obtained from Frontier Chemical and Pressure Chemical, respectively. Mercaptopropyl trimethoxysilane (MPTMS) was obtained from Fluka, and was used as

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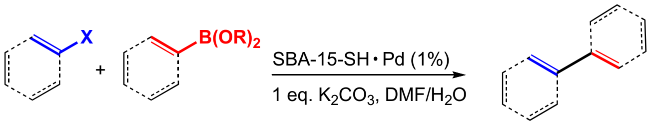


Scheme 1. The Suzuki–Miyaura cross-coupling reaction.

received. Solvents were of Certified A.C.S. grade and used as received, though DMF (Aldrich) was deoxygenated with bubbling Ar (g) prior to use.

2.2. Synthesis of mesoporous silica materials

SBA-15 was synthesized as previously reported [11,22]. Typically, 4 g of P123 was dissolved in acidic water (pH ~2) before the addition of the silica source (9 mL TEOS). Condensation of the silica network about the polymer template proceeded for 20 h at 35 °C before being treated hydrothermally at 80 °C for 48 h in a sealed vessel. Surfactant was removed from the as-made material by either calcination (1 °C/min ramp, 550 °C for 6 h) or extraction with ethanol. SBA-15-NaCl-type materials were synthesized in similar fashion, with 5 g of NaCl being added to the acidic solution before the addition of the silica source. Aluminum was incorporated into both SBA-15- and SBA-15-NaCl-type materials by adding 0.153 g $NaAlO_2$ to the aqueous solution after 6 h of silica condensation, as reported by Li et al. [39]. Adjusting the pH to 5 proved to be crucial in obtaining stable materials, and was monitored using a digital pH meter. Hydrothermal treatment was continued for 24 h after pH adjustment.

MCM-41 was synthesized following known procedures [22]. A modified MCM-41 material was prepared by adding decane as a pore-swelling agent, and hydrothermally treating the as-made material in the mother liquor for 48 h at 80 °C to encourage thickening of the walls.

2.3. Organic functionalization of silica surface and catalyst formation

Thiol groups were tethered to the silica surface by dispersing the material in toluene that contained an excess of MPTMS and refluxing the mixture for 16 h. Sulfur content of the functionalized materials was determined by elemental analysis. Typical sulfur loadings were between 0.5 and 1.0 mmol S/g material, though higher loadings could be achieved by pre-hydrolyzing the silica surface prior to thiol addition. Sufficient $Pd(OAc)_2$ (Pressure Chemical) to afford a 2:1 S:Pd catalyst was then added as a solution in THF. After treatment with the thiolated material, the solution became colourless, consistent with the previously reported absorption of >99.99% of Pd from solution [7–9].

2.4. Heterogeneous Suzuki–Miyaura catalysis

In a typical reaction, 0.5 mmol of aryl bromide (bromoacetophenone) was reacted with a slight excess of phenyl boronic acid pinacolate ester (PhBpin, column) at 80 °C in 20:1 DMF:H_2O in the presence of K_2CO_3 and the Pd catalyst. Reaction progress was monitored via examination of aliquots obtained from the reaction mixture by GC (FID), using dimethoxybenzene as an internal standard and a calibration curve to quantify the FID response. The heterogeneous catalyst was recovered by filtration of the reaction mixture and washing the collected solids with copious amounts of EtOAc and H_2O.

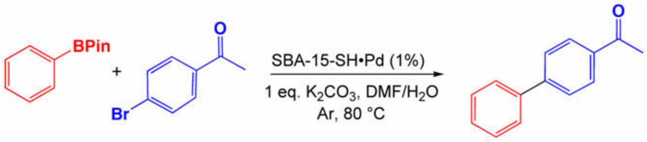
2.5. Material characterization

The degree of order and porosity of the synthesized materials and recycled catalysts was ascertained through nitrogen sorption analysis at 77 K using a Micromeritics ASAP2010 instrument. Sample degassing was performed at room temperature for all catalysts to prevent thermal decomposition of the attached organics and Pd catalysts. TEM images and Powder X-Ray Diffraction patterns were obtained on a JEOL 2011 Scanning TEM and Philips XRD System, respectively.

3. Results and discussion

3.1. Effect of Suzuki–Miyaura reaction conditions on silica structure

The use of thiol-functionalized mesoporous silicas as supports for Pd catalysts has provided leach-resistant, recyclable catalysts that are capable of affecting a variety of coupling reactions with minimal leaching. However, preliminary studies of material stability under typical Suzuki–Miyaura conditions indicated that material degradation occurred more quickly than under simple hydrothermal conditions [7–9]. Unlike other cross-coupling reactions such as the Sonogashira et al. [18] or Stille [19] reactions, the Suzuki–Miyaura reaction [2,3] (Eq. (1)) requires aqueous base to activate the boronate ester component [20]. Considering the known sensitivity of silica-based materials to an aqueous base [21], we targeted this component as a likely source of material degradation.



(1)

In order to test the stability of various materials to the reaction conditions without sacrificing large quantities of the organic substrates, a set of conditions was developed to emulate the Suzuki–Miyaura reaction. These conditions consisted of stirring the insoluble silica at 80 °C in 20:1 DMF:H_2O under inert atmosphere in the presence of the slightly soluble K_2CO_3 in the absence of reaction substrates. When tested under these *pseudo-reaction* conditions, both MCM-41 [22] and SBA-15-type materials lost their mesoporosity in *under 4 h*, illustrating the dichotomy between the hydrothermal conditions typically used to assess material stability and Suzuki–Miyaura cross-coupling reaction conditions [23]. For the subsequent stability studies, we employed SBA-15 prepared in the presence of NaCl (so-called SBA-15-NaCl), which

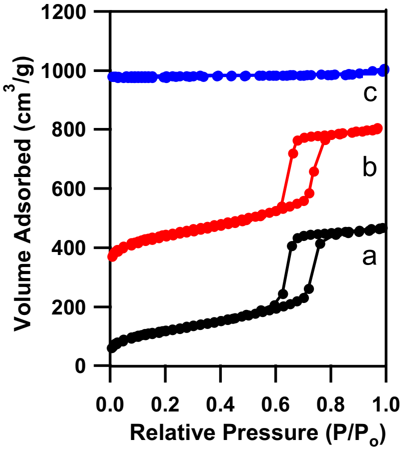


Fig. 1. Effect of base on the structure of an ordered mesoporous silicate. (a) SBA-15-NaCl (b) SBA-15-NaCl heated in 20:1 DMF: H_2O, 8 h (c) SBA-15-NaCl heated with base.

provides a more sensitive material that would permit us to rapidly screen different reaction conditions [24]. The results obtained in this study were then applied to SBA-15 prepared in the absence of NaCl.

The drastic effect of aqueous base is clearly demonstrated in Fig. 1. After 8 h of treatment with DMF/water at 80 °C (typical reaction temperature), there was no loss of order (compare Fig. 1a and b). However, upon addition of base, the pore structure of SBA-15-NaCl underwent complete collapse (Fig. 1c).

Although it is clear that the hot aqueous base is the main cause of material degradation, we were surprised to find that all the materials tested showed significantly *higher stability under actual reaction conditions than under pseudo-conditions using the same amount of base*. Consistent with this, the use of the filtrate from a completed Suzuki–Miyaura reaction as a solvent instead of freshly prepared 20:1 DMF:H_2O provided the same protective effect. These facts prompted us to systematically investigate the effect of reaction side products on material stability. A material exposed to KBr in the presence of base showed a similar rapid degradation (compare Fig. 2a and c). However, the addition of the other major side product, boric acid, resulted in virtually complete retention of porosity (Fig. 2b) and long-range order confirmed by pXRD (Fig. 3).

The effect of boric acid was also found to be concentration dependent, with the best results being observed with >1 equivalent [25]. The consequence of this under actual reaction conditions is that reactions that quickly attain high conversion of the organic substrates (producing boric acid as a side product) will result in greater material stability compared to those that react more slowly [26]. Although adding boric acid at the beginning of every run was an effective strategy to stabilize the material, we decided to examine the direct incorporation of a similar group 13 element, aluminum, directly into the material. Although boron-containing mesoporous materials have been described in the literature [27–32], the hydrothermal stability of aluminum-containing materials has received significantly greater attention due to the interest in preparing mesoporous materials with high-acidity for cracking applications [33–38]. Al-doped mesoporous materials have been reported to have remarkable stability under hydrothermal conditions (300 h in boiling water and 6 h of steaming at 600 °C) [39], however, stability to aqueous base has not been examined.

Several rationales have been proposed for the stabilizing effect of aluminum [40]. When incorporated into the walls of mesoporous materials, the so-called “structural Al” decreases the overall order of the material [41], making it thermodynamically more stable [40]. Additionally, since structural Al is tetra-coordinated, it imparts an anionic character to the aluminosilicate wall, protecting the surface from attack by hydroxide [42,43], which is the starting point for degradation by hydrolysis of Si–O–Si bonds [44]. Even extra-framework, octahedral Al is proposed to have a protective effect, by reacting with surface silanols, protecting them and also reactive siloxane bridges, from attack by base [43]. Shen and Kawi demonstrated this conclusively by coating the surface of preformed all-silica MCM-41 with Al_2O_3, which resulted in a material that still retained high surface area after one week in boiling water [40].

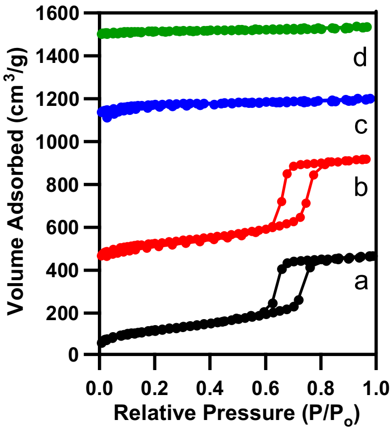


Fig. 2. Effect of major side products of the Suzuki–Miyaura reaction on material stability. (a) Pristine SBA-15-NaCl; (b) SBA-15-NaCl heated with base and 2 eq. of $B(OH)_3$ (c) SBA-15-NaCl heated with base and KBr; (d) SBA-15-NaCl heated with base.

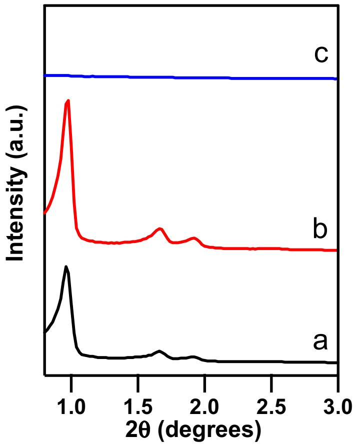


Fig. 3. XRD patterns of ordered mesoporous silicate and effect of boric acid on stability. (a) Pristine SBA-15-NaCl; (b) SBA-15-NaCl heated with base and 2 eq. $B(OH)_3$. (c) SBA-15-NaCl heated with base alone.

Aluminum-doped SBA-15 [33,45] was prepared following the method of Li et al. [39] in the hope that it would also show resistance to aqueous base. Li et al. showed that the stability of the material prepared by incorporating Al during materials synthesis depended strongly on both the temperature and the pH of the mother liquor during hydrothermal treatment, with the sturdiest materials being prepared at pH 5 and temperatures in excess of 100 °C [39]. Using these conditions, we prepared aluminum-doped ordered materials, which will be designated Al-SBA-15. The presence of a large signal at 52 ppm in the ^{27}Al NMR of all doped materials indicates that aluminum is primarily in a tetrahedral arrangement, bound to four silicon centers through siloxane bonds [14,46]. However, the broadness of this signal makes it difficult to rule out the presence of small amounts of extra-framework octahedral aluminum. During exposure to reaction conditions, the tetrahedral form of aluminum becomes more prevalent, indicating that the extra-framework Al is being either removed from the material, or incorporated during the reorganization of the silicate wall structure. As will be shown in the following section, these materials have greater stability under the reaction conditions than SBA-15 itself, consistent with the greater hydrothermal stability reported for Al-doped mesoporous materials [34,40,46–48].

3.2. Catalysis on mesoporous silicate supports

Having gained an understanding of the factors affecting the stability of the material, we examined derivatized versions of these materials as catalysts for the Suzuki–Miyaura reaction under actual reaction conditions. In order to retain Pd on the various supports, the surface was first treated with mercaptopropyl trimethoxysilane (MPTMS) to provide a ligand for Pd [49]. This type of thiolated material has been shown by our group and others to be a superb scavenger for Pd, reducing 500 ppm solutions to a few ppb [8,50]. After the absorption of Pd, the resulting materials function as effective, leach-resistant catalysts depending on the S:Pd ratio. In order to minimize leaching and maximize activity, the S:Pd ratio should be ca. 2:1. At lower ratios, Pd leaching becomes more significant, and at higher ratios, the catalyst is inactive [7].

3.2.1. MCM-41 Pd catalysts

With wall thicknesses of only ∼10 Å, and short lifetimes demonstrated in the *pseudo*-studies, thiol-functionalized MCM-41 Pd catalysts (henceforth MCM-41-SH·Pd) were not expected to be highly reusable catalysts. Near quantitative conversions for the first two cycles (Fig. 4) indicated that catalysis is not limited by the smaller pore size of MCM-41 materials, though a sudden loss of activity is observed during the third run (see Fig. 4).

Examination of the material's structural integrity over time (Fig. 5) indicated that the MCM-41-SH Pd catalyst underwent almost complete degradation after less than 5 h of use in the Suzuki–Miyaura reaction. Thus in the case of MCM-41, the stabilizing effect of boric acid produced during the reaction is unable to overcome the fragility of the thin, ca. 10 Å, walls. The most interesting fact gleaned from this study was that in all cases, *the loss of activity occurred concurrently with the loss of pore structure*. Our group has previously shown that active catalysts can be made with amorphous silica [7], therefore, the long-range order is not necessary for catalysis, but porosity is necessary. Thus it appears that loss of order in a support which was mesoporous to begin with results in a complete loss of catalytic activity. This likely occurs by the trapping of active Pd species in the collapsed pore structure. The same effect was observed using meta-stable NaCl-doped SBA-15-based catalysts as shown in Fig. 6. Loss of catalytic activity was concomitant with loss of order.

Various methods have been described to improve the hydrothermal stability of MCM-41, including hydrothermal restructuring [51]. the addition of inorganic salts during the synthesis [52,53], and doping alumina into the material [14,33,34,39–41,43,45–48]. Thus the effect of hydrothermally treating MCM-41 after silica condensation (H_x MCM-41-SH·Pd, 0.77 mmol S/g material) was examined. Although the catalyst showed a similar activity in the Suzuki–Miyaura coupling, hydrothermal treatment did not afford an increase in stability over the course of multiple uses. Materials with higher thiol content were also prepared (MCM-41-xSH·Pd, 1.50 mmol S/g material) in the hope that the increased organic functionality would protect the surface by rendering it more hydrophobic [54]. Again, only slight improvements of the material stability were observed. Considering these facts, we focused our attention on the thicker-walled SBA-15-type materials.

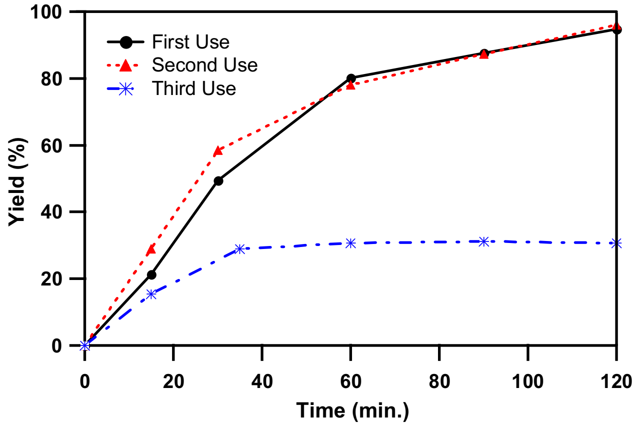


Fig. 4. MCM-41-SH·Pd Suzuki cross-coupling recycle study.

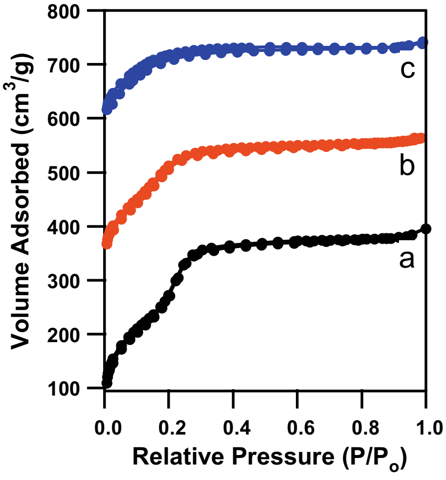


Fig. 5. N_2 isotherms of MCM-41-SH·Pd catalyst and subsequent uses in Suzuki coupling reactions. (a) Pristine catalyst; (b) first use and (c) third use.

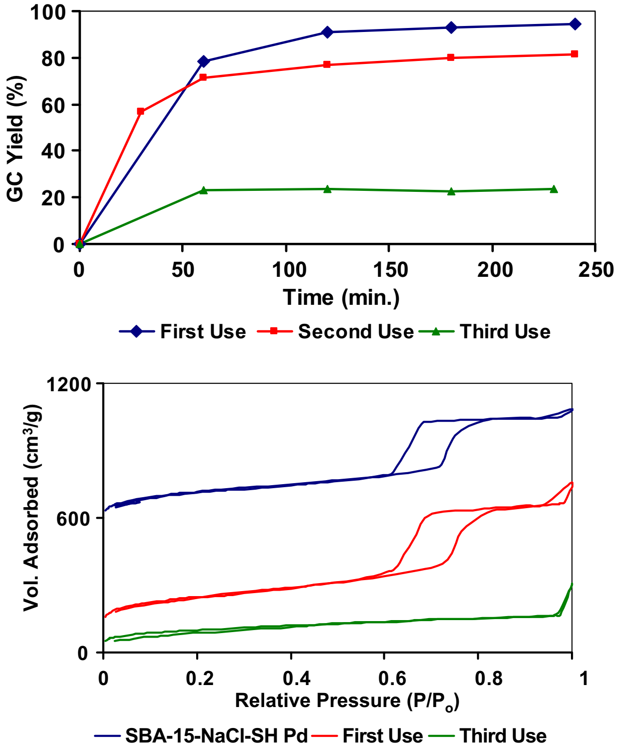


Fig. 6. N_2 isotherms of SBA- NaCl-15-SH·Pd catalyst and subsequent uses in Suzuki coupling reactions.

3.2.2. SBA-15 Pd catalysts

When coupled with the stabilizing effect of boric acid, the substantially thicker walls of SBA-15 were better able to withstand the harsh reaction conditions than MCM-41 based materials. This translated to a higher reusability of SBA-15-derived Pd catalysts with SBA-15-SH·Pd, (0.62 mmol S/g material), which remained ordered and catalytically active for a considerably longer time. As shown in Fig. 7, the catalyst retains virtually all of its order after three runs, corresponding to a total of 24 h, although a slight drop in catalytic activity is observed in the last run.

As Al-SBA-15 is reported to have improved hydrothermal stability compared to regular SBA-15 [33,34], we were optimistic that it would serve as a rugged support for Pd catalysis. Indeed, the

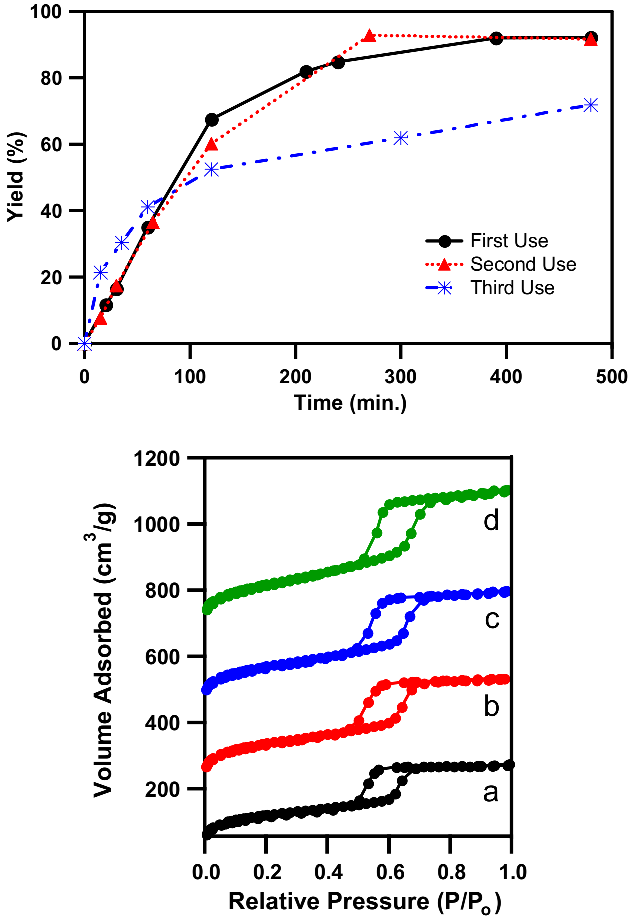


Fig. 7. Suzuki–Miyaura conversion (top) and N_2 isotherms (bottom) for SBA-15-SH·Pd catalyst. (a) Pristine SBA-15. After first (b), second (c) and third (d) uses.

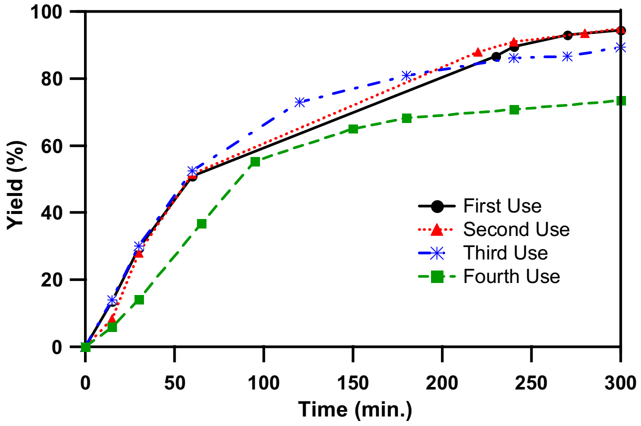


Fig. 8. Conversions for series of Suzuki reactions catalyzed by Al-SBA-15-SH·Pd.

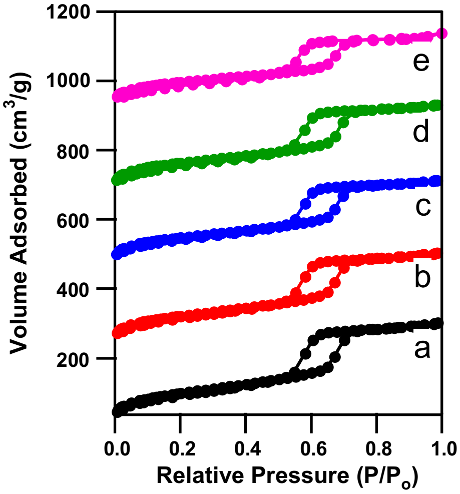


Fig. 9. N_2 isotherms for four consecutive uses of Al-SBA-15-SH·Pd in the Suzuki Reaction. (a) Pristine Catalyst. (b)–(e) First to fourth use of catalyst.

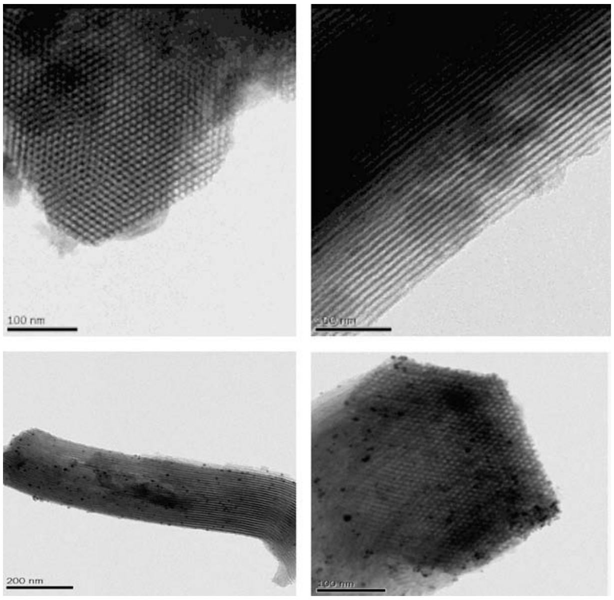


Fig. 10. TEM images of pristine Al-SBA-15-SH·Pd (top) and Al-SBA-15-SH·Pd after four recycles totalling 20 h under Suzuki–Miyaura conditions (bottom).

Al-SBA-15-SH·Pd (1.79 mmol S/g material) catalyst also remained well ordered over 20 h of Suzuki reaction time and, unlike the SBA-15-SH·Pd catalysts, retained full catalytic activity throughout the course of the entire recycle sequence (Figs. 8 and 9). Examination of the material by TEM (Fig. 10) showed that the Al-SBA-15-SH·Pd catalyst is still highly ordered after 20 h of use. The observation of Pd nanoparticles by TEM, seen as dark spots in the pores of the material and occasionally on the exterior, is consistent with our previous studies of SBA-15-SH·Pd [7]. XRD analysis of a second series of recycles confirms that the long-range order of the material is maintained after three catalyst uses, although the intensity of the 100 signal is decreased compared with pristine material, Fig. 11.

3.3. Assessment of leaching

With information about support stability and reusability in hand, the next important factor to be determined was leaching of Pd. In our previous work we showed that pure silica-based materials functionalized by MPTMS were able to affect the Suzuki–Miyaura coupling shown in Eq. (2) with extremely low levels of leaching. As ppm is a concentration-dependent measurement, we prefer to report the Pd leaching as a percentage of initially added Pd. We should note, however, that in all cases the solutions at the end of the reaction were less than 0.5 ppm, and were often in the low ppb range.

Thus it was necessary to determine whether or not the incorporation of aluminum into the material had any deleterious effect on

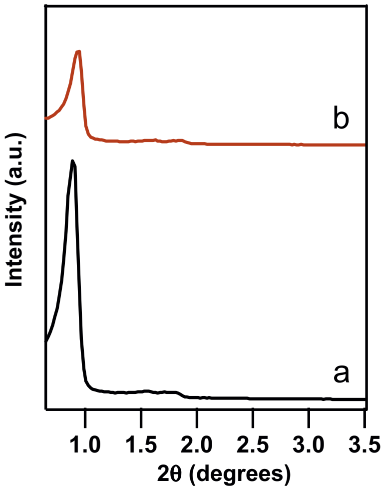
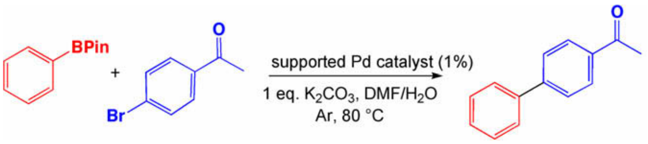


Fig. 11. (a) XRD pattern of pristine Al-SBA-15.Pd and (b) after three uses totalling 15 h under Suzuki–Miyaura conditions.

Table 1
Pd leaching from thiolated mesoporous materials with and without Al.



(2)

Entry	Support material	S:Pd ratio	Yield (%)	Pd leaching (%)
1	Al-SBA-15-SH	2:1	99	0.02
2	SBA-15-SH	2:1	98–99	0.12
3	SiO_2-SH	2:1	98	0.06
4	Al-SBA-15-SH	1.75:1	99	0.16
5	SiO_2-SH	1:1	86	0.3

Pd retention on the material. In order to examine this, our test reaction was performed with the Al-containing thiolated Pd catalyst. As previously determined, matching the Pd loading to the thiol content is critical in order to obtain a material that is catalytically active without leaching Pd into solution at the completion of the reaction [7]. Thus as shown in Table 1, the material prepared with a sulfur:Pd ratio of 2:1 (which was catalytically active) retained 99.98% of the initially added Pd on support at the end of the reaction. In fact, the Al-containing material was marginally superior to catalysts prepared from SBA-15 itself or amorphous silica (compare entries 1, 2, and 3), although all three supported catalysts can be considered to be acting with the same basic level of leaching.

A catalyst prepared with slightly higher levels of Pd still performed well, although as expected (entry 5), slightly higher leaching (0.16%) was observed. In both the examples using Al-SBA-15-SH as the support, the Pd content of the solution was in the low ppb range.

4. Conclusions

Although the application of mesoporous materials in a range of catalytic reactions is increasing, in order to employ these materials in diverse reactions, their stabilities under a variety of reaction conditions need to be assessed. We have shown that the basic conditions of the Suzuki–Miyaura reaction lead to a rapid and deleterious reordering of otherwise stable mesoporous silicate materials. This degradation is mitigated by the formation of boric acid as a reaction side product. A strengthening effect could be achieved by doping aluminum into the material, producing a material with dramatically increased stability to the reaction conditions. Thiol functionalization and Pd loading of the stable aluminosilicate material yielded a highly active and reusable catalyst, one that retained its mesoporosity and long-range order over the course of multiple recycles. By performing catalytic runs and material analysis in concert, we were able to show that catalytic activity is lost when the material structure degrades. Finally, the examination of Pd leaching at the completion of the reaction indicated that the Al-incorporated material was at least as good as, if not better than the regular SBA-15-based thiolated catalysts that were prepared previously by our group.

Acknowledgments

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Appendix A. Supplementary material

^{27}Al, ^{29}Si MAS NMR spectra and concentration dependence of boric acid effect on silicate stability. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2009.04.020.

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