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## Pronounced effect of pore dimension of silica support on Pd-catalyzed Suzuki coupling reaction under ambient conditions

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### Abstract

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Pore size of the mesoporous silica support is found to have enormous effect on the reactivity of the Pd-catalysts in Suzuki coupling reaction. Heterogeneous palladium catalysts, **MCM-Pd** and **SBA-Pd**, have been synthesized using two different types of silica supports which differ from each other in their pore dimension. The silica surfaces are grafted with aminopropyl silane groups and functionalized with *tris*(4-formylphenyl)amine engaging one of the formyl groups while the other two formyl groups are reacted with two 2-aminothiophenol moieties. This gives rise to two Schiff base sites with adjacent –SH groups leading to active metal binding sites in the samples and increases hydrophobicity of the framework. The materials have been characterized by powder X-ray diffraction, nitrogen sorption studies, transmission electron microscopy, thermal analysis, and different spectroscopic techniques. The samples are used as catalysts for Suzuki cross-coupling reactions of aryl halides with phenylboronic acid at ambient condition. The products of the reactions are identified and estimated by <sup>1</sup>H NMR and gas chromatography. **SBA-Pd** performs much better compared to **MCM-Pd** and yield up to 98% is achieved in CH<sub>3</sub>OH within 24 h of the reactions. This is attributed to the higher pore dimension of **SBA-Pd** that allows better interaction of the substrate molecules with the active centers on the surface of the pores.

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### Introduction

Organic transformations catalyzed by transition metal have gained widespread attention over the years as they yield valuable products and new functional groups can be introduced into relatively inert substrates. Palladium catalyzed Suzuki cross-coupling reaction for the formation of the C-C bond is one such commercially important reaction which has been extensively studied since its first report in 1979.<sup>1,2</sup> It has enormous importance in synthetic organic chemistry<sup>3</sup> and different catalytic systems for this reaction have been reported in the literature.<sup>4-6</sup> However, most of the catalytic studies have been carried out in homogeneous systems using palladium complexes that are soluble in reaction media.<sup>7,8</sup> Though homogeneous catalysts generally require lower temperature than heterogeneous catalysts they have serious disadvantages, like complicated recovery and regeneration process of the expensive catalyst.<sup>9-12</sup> But for heterogeneous catalysis, the catalyst being in a different phase in the reaction media, separation of the product and the catalyst can be done easily, mostly simply by filtration or centrifugation. Thus, heterogeneous catalysts can be recycled and reused for several reaction cycles without significant loss in their structure or reactivity. Thus, efforts have been made to design safe, effective and recyclable heterogeneous catalysts for a number of reactions, including C-C bond formation reactions.<sup>13,14</sup> However, leaching of metal ion into the reaction media remains a drawback of heterogeneous catalysts. In such cases it becomes difficult to conclude on the heterogeneity of the catalyst as then it can be both the metal ions leached in to solution or bound to the solid support that catalyzes the reaction. Thus, the metal ion should be strongly bound to the solid support such that it does not dissociate from the framework during the liquid phase catalytic reactions.

To prepare a heterogeneous catalyst, a solid support in which the functional groups can be introduced and the metal atoms can be strongly immobilized is necessary. Different types of catalyst supports are known in the literature. Some of them include zeolite,<sup>15</sup> alumina,<sup>16</sup> silica,<sup>17-19</sup> polymer,<sup>20-22</sup> mesoporous carbon,<sup>23,24</sup> carbon nanotubes,<sup>25,26</sup> graphene,<sup>27,28</sup> metal-organic framework,<sup>29,30</sup> metal oxide nanoparticles,<sup>31,32</sup> immobilized nanoparticles,<sup>33,34</sup> *etc.*<sup>35,36</sup> Among these, mesoporous silica is often chosen as a catalyst support for its numerous advantages like high surface area, large pore volume and precise tuning of pore size according to requirement.<sup>37</sup> These properties allow suitable interaction of the substrate with the active centers on the surface of the catalyst and increases the efficiency.<sup>13</sup> Moreover, silica framework is rigid, thermally and chemically stable, and modification can be easily done to introduce different functional groups that enable strong binding of metal ion. A large number of organic precursors have been used for the synthesis of organically modified hybrid mesoporous silica, to functionalize their surface and induce hydrophobicity.<sup>38,39</sup> They bear suitable donor sites that efficiently bind metal centers through covalent bonding. The nature of interaction between the metal center and the pore-wall make the materials extraordinarily stable and minimize the possibility of metal leaching during catalytic reactions.

For Suzuki cross-coupling reactions, most of the research has been carried out on development in reaction scope, like use of aryl chlorides,<sup>40,41</sup> non-activated halides<sup>42</sup> and esters<sup>43</sup> as substrates, selection of boron reagents for the reactions,<sup>44</sup> effect of ligand<sup>45, 46</sup> and ligand free conditions,<sup>47</sup> ability to carry out reaction at ambient

temperature,<sup>48, 49</sup> in aqueous medium,<sup>21,47,49,50</sup> under solvent-free conditions,<sup>51</sup> in green solvents,<sup>52</sup> with very low catalyst loadings,<sup>53, 54</sup> *etc.* But, to the best of our knowledge, there are so far no systematic studies reported that deal with the effect of the pore size of the mesoporous silica support on the activity of Pd-catalysts in Suzuki coupling reaction. Since the functionalization of the organics and hence anchoring of the metal centers take place inside the pores of the mesoporous framework, the residual pore space plays an important role in determining the catalytic performance. It is known that catalytic activity improves with greater surface exposure of the substrates to the active centers and their accessibility into the porous structure. Temperature also plays an important role here, as in any reaction, by providing the activation energy; higher the temperature faster is the reaction. Hence at higher temperatures it is difficult to carry out comparative study of catalysis using systems that differ only in their pore structure. Thus, catalytic systems studied at room temperature, with judicial choice of donor atoms that binds strongly with specific metal ions and differing only in pore dimension can add substantially to the understanding of such C-C bond formation reactions.

In this respect, we have synthesized, characterized and studied heterogeneous catalytic properties of two palladium immobilized mesoporous silica materials, MCM-Pd and SBA-Pd (Scheme 1). The two silica supports used for this study belong to two different families of silicates. While the MCM-41 type silica<sup>55</sup> with pore diameter of *ca*. 3.8 nm is synthesized using ionic surfactant template, the SBA-15 silica<sup>56</sup> with 7.6 nm size is prepared using a non-ionic block-copolymer template. The silica surfaces are grafted with aminopropyl silane molecties and functionalized with trialdehyde, *tris*(4-formylphenyl)amine employing one of the aldehyde groups. Incorporation of the bulky organic moiety enhances hydrophobicity of the silica framework and checks its hydrolysis in polar solvent. The other two aldehyde groups are allowed to undergo Schiff-base condensation with 2-aminothiophenol which results in introduction of multiple imine-N and thiol –SH groups in the mesopore wall. These donor atoms can bind strongly to the palladium species and the soft sulfur center preferentially stabilizes the soft metal.<sup>57,58</sup> Introduction of two binding sites in one functional system in contrast to other systems reported earlier<sup>19,21</sup> with one binding site per functionality increases the number of active sites available for metal binding. The sequential steps of functionalization and metal loading lead to reduction in the mesopore volume in the materials. The objective of this work is to study the reactivity of the two heterogeneous catalysts which differ in their pore structure in Suzuki coupling reactions at room-temperature. It is indeed found that the pore size and volume has a huge effect on the catalytic properties.

#### **Experimental**

### Materials and physical measurements

All chemicals used in the syntheses are obtained from commercial sources and used without further purification. The Powder X-ray diffraction patterns of the samples have been collected on a Bruker D-8 Advance instrument using Ni-filtered Cu-K $\alpha$  radiation ( $\lambda = 1.5406$  Å) operated at 40 kV and 40 mA. Nitrogen sorption isotherms of the samples are measured at 77 K using a NOVA 2200e Surface Area and Pore Size Analyzer, Quantachrome Instruments, USA. Prior to the measurements, the samples are degassed for 8-12 h at 393 or 423 K depending on the nature of the framework and the specific surface areas are obtained from the isotherms using Brunauer-Emmett-Teller (BET) and Langmuir method. For the pore size distribution profiles, non-local density functional theory (NLDFT) model has been used. The transmission electron microscopic (TEM) images have been recorded in a JEOL JEM-1400 transmission electron microscope. Before the analysis sample grids have been prepared by putting one drop of the samples dispersed in  $C_2H_3OH$  on a thin layer of amorphous carbon coated copper grid of 400 mesh. FT-IR spectra of the samples at different stages have been recorded on a Perkin Elmer spectrometer (Spectrum Two) using attenuated total reflectance (ATR) technique. Solid state <sup>13</sup>C CP and <sup>29</sup>Si MAS NMR analyses are carried out in a CHEMAGNETICS 300 MHz CMX 300 spectrometer. Thermogravimetric studies have been done under nitrogen atmosphere (flow rate: 50 cc/min) from room temperature to 1200 °C (heating rate of 2 °C/min) using a Perkin Elmer STA -6000 thermal analyzer. Palladium contents of the samples are measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Shimadzu ICPS-7510 Sequential Plasma Spectrometer. The solutions for analyses are prepared by digesting 30 mg of the samples in 1 mL of hydrofluoric acid to dissolve the silica part followed by the addition of 1 mL of nitric acid, which solubilizes the materials completely. The volumes are made up to 25 mL with Milli-Q water, the solutions are membrane filtered and fed into the auto-sampler of the spectrometer. Gas chromatography studies are carried out using a Shimadzu GC-2014 gas chromatograph equipped with a fused silica capillary column and a FID detector. <sup>1</sup>H and <sup>13</sup>C NMR spectra are recorded in CDCl<sub>3</sub> solvent using a Bruker 400 MHz spectrometer with tetramethylsilane ( $\delta = 0$ ) as the internal standard. The chemical shifts are expressed in parts per million ( $\delta$ ).

### Syntheses of the catalysts

Syntheses of mesoporous MCM-41 and SBA-15 mesoporous silica and their functionalization with 3-aminopropyl triethoxy silane

For the synthesis of MCM-41,<sup>55</sup> an acidic aqueous solution was made by dissolving 0.78 g of tartaric acid in 60 g of water. Then 2.96 g of cetyltrimethylammonium bromide (CTAB) and 1.5 g of Brij-35 ( $C_{12}H_{12}$  ( $OC_{2}H_{4}$ )<sub>23</sub>OH), a polyether and aliphatic hydrocarbon chain surfactant) were dissolved in that acidic solution under stirring at room temperature for 30 minutes. Then 3.5 g of tetraethyl orthosilane was added drop wise to the mixture under

continuous stirring and the resulting gel was stirred for 2 h. Then 1(M) NaOH solution was added dropwise until the pH became approximately 11. The resulting white mixture was aged overnight under stirring at room temperature and then heated at 348 K for 72 h without stirring in a polypropylene bottle. The solid product was then recovered by filtration, washed several times with water, and dried under vacuum. The resulting powder was calcined in a flow of air at 723 K for 8 h for complete removal of the organic structure directing agent.

For synthesis of SBA-15,<sup>56</sup> 1.7 g of Pluronic P123 (a block copolymer, Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol)) was dissolved in 62 ml of water (taken in a polypropylene bottle) under stirring. 6 g of 35% HCl was added to the resulting clear solution and stirred again. Then 3.5 g of tetraethyl orthosilane was added drop wise to the mixture and stirred at 313 K for 20 h. The resulting gel was then aged at 373 K for 20 h without stirring. After cooling to room temperature, the product was isolated by filtration and washed repeatedly with water and  $C_2H_5OH$  and dried at 373 K. The mesoporous silica was then obtained as a white powder after calcination at 773 K in a flow of air.

Both the mesoporous silica materials, MCM-41 and SBA-15 were functionalized with 3-aminopropyl triethoxy silane (3-APTES) by stirring 0.5 g of the respective silica with 0.9 g of 3-APTES for 12 h in chloroform at room temperature under  $N_2$  atmosphere. The ethoxy groups of 3-APTES condense with the residual –OH groups on the surface of the mesoporous silica. The white solid 3-aminopropyl functionalized MCM-41 and SBA-15 were obtained after filtering the suspension, washing the product repeatedly with chloroform followed by dichloromethane and drying in air.<sup>59</sup>

## Grafting of tris(4-formyl phenyl) amine on 3-aminopropyl triethoxy silane functionalized MCM-41 and SBA-15 silica

The trialdehyde, *tris*(4-formyl phenyl) amine, has been synthesized through Vilsmeier-Haack formylation reaction of triphenylamine following a reported procedure.<sup>60</sup> The 3-APTES functionalized MCM-41 silica was refluxed with the trialdehyde dissolved in CH<sub>3</sub>OH for 4 h (Scheme 1). The mole ratio of amine to trialdehyde was kept 1:1 so that only one formyl group undergoes Schiff base condensation with the 3-APTES amine and the remaining formyl groups in each molecule stay unreacted. The resulting light yellow solid was collected through filtration, washed repeatedly with CH<sub>3</sub>OH until the filtrate become colorless and finally dried in a vacuum desiccator. Similar process was carried out with 3-APTES functionalized SBA-15 silica to get the corresponding *tris*(4-formyl phenyl) amine Schiff-base product.

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Scheme 1. Grafting of *tris*(4-formyl phenyl) amine on 3-aminopropyl triethoxy silane functionalized silica and Syntheses of MCM-Pd and SBA-Pd

## Incorporation of –N and –S donor sites into tris(4-formyl phenyl) amine grafted mesoporous silica and synthesis of the catalysts, MCM-Pd and SBA-Pd

The *tris*(4-formyl phenyl) amine grafted mesoporous MCM-41 silica was treated with 2-aminothiophenol which undergo Schiff base condensation with the two unreacted –CHO groups (Scheme 1). 2-aminothiophenol was taken two times with respect to *tris*(4-formyl phenyl) amine and the suspension in CH<sub>3</sub>OH was stirred for 6 h at room temperature. The dark yellow material was recovered by filtration, washed with CH<sub>3</sub>OH and dried in a vacuum desiccator. In a similar way, *tris*(4-formyl phenyl) amine grafted mesoporous SBA-15 silica was also functionalized with 2-aminothiophenol.

1.0 g of each of the 2-aminothiophenol functionalized silica materials are stirred for 2 h with 0.1 g of palladium acetate dissolved in 20 mL of CH<sub>3</sub>OH at room temperature. The dark brown solid catalysts formed were filtered and washed with CH<sub>3</sub>OH to remove any unreacted salt and dried under vacuum. The Pd-immobilized materials thus obtained are named as **MCM-Pd** and **SBA-Pd** when the silica support is functionalized MCM-41 and SBA-15, respectively.

**Catalysis:** To determine the efficiency of **MCM-Pd** and **SBA-Pd** catalysts in Suzuki coupling reaction several parameters like solvent, base and reaction time have been explored. In a typical catalytic cycle, 1.0 mmol of the aryl halide, 1.2 mmol of aryl boronic acid and 2.5 mmol of base were taken in 10 mL of solvent and the mixture was stirred at room temperature. The reaction was started with the addition of 0.01 g of the catalyst. The reactions were continued for the desired time and the solid catalyst was separated from reaction mixture by centrifugation. Then products were extracted in diethyl ether and organic layer was repeatedly washed with brine solution and water. The solvent was evaporated, the product was purified using column chromatography and from here isolated yield was recorded. Finally the compounds were characterized by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> solvent. Beside <sup>1</sup>H NMR analyses, gas chromatography studies are also carried out to identify the products formed, determine the yield and turnover frequencies. For reusing the catalysts, the solid separated by centrifugation was washed repeatedly and then stirred with C<sub>2</sub>H<sub>3</sub>OH at room temperature for 2 h to remove any adhered organic compound from the previous catalytic cycle. After drying, the catalysts was checked by performing filtration tests. For that the catalysts were separated from the reaction mixture after 2 h and then the reactions were continued for the typical duration.

### **Results and Discussion**

The microstructure of the samples prepared over two different types of supports has been carried out using powder X-ray diffraction study. There are two set of data; one for the MCM-41 series of samples and the other for the SBA-15 series. The patterns for calcined MCM-41, 3-APTES functionalized MCM-41, *tris*(4-formyl phenyl) amine loaded MCM-41and **MCM-Pd** are given in Fig. 1. The corresponding diffraction patterns for the SBA-15 family of samples along with **SBA-Pd** are given in Fig. 2. Both set of samples show 2D-ordered hexagonal mesostructure that is indicated by the presence of three distinct diffraction peaks and can be assigned to 100, 110 and 200 planes along with a weak signal for 210 plane.<sup>61, 62</sup> However, with gradual functionalization the ordering of pores decreased somewhat along with reduction in pore size; these are reflected from the lowering of peak intensities and shifting of the peaks to higher 20 values, respectively. The diffraction patterns of **MCM-Pd** and **SBA-Pd**, obtained by attaching 2-aminothiophenol moiety to the functionalized supports and then loading palladium centers over them, remain almost unchanged as compared to the functionalized support which indicates that there is no significant shrinkage in size of the pores. However, the intensity of the peaks reduces to some extent, which is again attributed to the lowering of ordering of the pores in the samples in comparison to the silica support used for further functionalization.



**Fig. 1.** Powder X-ray diffraction patterns of (a) calcined MCM-41, (b) 3-APTES functionalized MCM-41, (c) *tris*(4-formyl phenyl) amine loaded MCM-41 and (d) **MCM-Pd**.



Fig. 2. Powder X-ray diffraction patterns of (a) calcined SBA-15, (b) 3-APTES functionalized SBA-15, (c) *tris*(4-formyl phenyl) amine loaded SBA-15 and (d) SBA-Pd.

SI. No.	Sample	BET Surface Area (m²/g)	Langmuir Surface Area (m²/g)	Pore Volume (cc/g)	Pore Size (nm)
(a)	MCM-41	963	1422	1.548	3.78
(b)	3-APTES functionalized MCM-41	505	838	0.794	2.95
(c)	Tris(4-formyl phenyl) amine loaded on (b)	241	375	0.576	2.59
(d)	2-aminothiophenol grafted on (c)	160	248	0.532	
(e)	MCM-Pd	140	222	0.408	
(f)	SBA-15	704	1091	0.958	7.588
(g)	3-APTES functionalized SBA-15	408	661	0.567	6.794
(h)	Tris(4-formyl phenyl) amine loaded on (g)	242	390	0.254	5.880
(i)	2-aminothiophenol grafted on (h)	177	291	0.27	
(j)	SBA-Pd	129	207	0.192	

Table 1: Surface area, pore volume and pore size of the samples at various stages

The nitrogen adsorption/desorption isotherms have been studied at various stages of functionalization of both kind of silica support which vary in their pore sizes. The isotherms for calcined MCM-41, 3-APTES functionalized MCM-41, tris(4-formyl phenyl) amine loaded MCM-41, 2-aminothiophenol grafted tris(4-formyl phenyl) amine MCM-41 and MCM-Pd are given in Fig. 3. The corresponding isotherms for calcined SBA-15, 3-APTES functionalized SBA-15, tris(4-formyl phenyl) amine loaded SBA-15, 2-aminothiophenol grafted tris(4formyl phenyl) amine SBA-15 and SBA-Pd are shown in Fig. 4. The BET (Brunauer-Emmett-Teller) and Langmuir surface areas, pore size and pore volume of the samples are given in Table 1. It can be seen in both the cases that gradual decrease in the surface area takes place after each stage of functionalization. The Langmuir surface areas are higher compared to BET surface areas which are attributed to the assumptions taken in the model chosen and the process involved in surface area determination. Both series of samples showed typical type IV isotherms with steep rise at higher pressure due to capillary condensation indicating the mesoporous nature of the materials.<sup>63, 64</sup> Desorption hysteresis is observed for MCM-41 based samples which arises from intercrystallite adsorption.<sup>65</sup> In case of SBA-15 set of samples, quite broad H<sub>1</sub>-type hysteresis can be seen typical of mesoporous materials with 1D cylindrical channels.<sup>66</sup> The average pore diameter of the starting mesoporous silica, MCM-41 and SBA-15 obtained by NLDFT model are *ca.* 3.8 and 7.6 nm, respectively (Fig. 5). As expected the size of the pore decreases gradually when functionalization takes place on the walls of the pores. This trend is also followed by the pore volume and it is noteworthy that though the pore sizes of SBA-15 based samples are higher the corresponding pore volumes are lower compared to the MCM-41 series of samples.



Fig. 3. Nitrogen sorption isotherms of (a) calcined MCM-41, (b) 3-APTES functionalized MCM-41, (c) *tris*(4-formyl phenyl) amine loaded MCM-41, (d) 2-aminothiophenol grafted *tris*(4-formyl phenyl) amine MCM-41 and (e) MCM-Pd. For clarity, Y-axis values have been made offset by 100 cc/g, 70 cc/g, 130 cc/g and 70 cc/g, for plot a, b, c and d, respectively. (Adsorption points: filled symbols; desorption points: empty symbols)



Fig. 4. Nitrogen sorption isotherms of (a) calcined SBA-15, (b) 3-APTES functionalized SBA-15, (c) *tris*(4-formyl phenyl) amine loaded SBA-15, (d) 2-aminothiophenol grafted *tris*(4-formyl phenyl) amine SBA-15 and
(e) SBA-Pd. For clarity, Y-axis values have been made offset by 100 cc/g, 70 cc/g, 50 cc/g and 50 cc/g, for plot a, b, c and d, respectively. (Adsorption points: filled symbols; desorption points: empty symbols)



Fig. 5. Pore size distribution of (a) MCM-41 and (b) SBA-15 using NLDFT model

The BET surface areas of the 2-aminothiophenol grafted *tris*(4-formyl phenyl) amine MCM-41 and **MCM-Pd** are 160 and 140 m<sup>2</sup>g<sup>-1</sup>, and the pore volumes are 0.532 and 0.408 cc/g, respectively (Table 1). For the 2-aminothiophenol grafted *tris*(4-formyl phenyl) amine SBA-15 and **SBA-Pd**, the BET surface areas are 177 and 129 m<sup>2</sup>g<sup>-1</sup>, and the pore volumes are 0.270 and 0.192 cc/g, respectively. The basic character of the samples remains the same; with type-IV isotherms for all and broader hysteresis for SBA-15 based materials than the corresponding MCM-41 types. However, the pore sizes of these samples obtained using NLDFT model is very conclusive. This may happen due to anchoring of excessive functional groups on the pore surface of the silica support which hinders the access of nitrogen molecules for adsorption on the surface of mesoporous silica. However, the TEM images of the samples (shown below) confirm that the basic hexagonal arrangement of pores is retained in the silica supports after all the functionalization and metal loading process.

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**Fig. 6.** TEM images of (a) **MCM-Pd**, (b) **SBA-Pd**, (c) *tris*(4-formyl phenyl) amine loaded MCM-41 and (d) *tris*(4-formyl phenyl) amine loaded SBA-15

The TEM images of **MCM-Pd** and **SBA-Pd**, obtained after successive functionalization of MCM-41 and SBA-15, respectively, have been illustrated in Fig. 6 (a and b, respectively). Both the samples show hexagonal arrangement of pores having a different contrast with respect to the pore walls. The TEM images of samples at an intermediate step after *tris*(4-formyl phenyl) amine is loaded on MCM-41 and SBA-15 has been illustrated in Fig. 6 (c and d, respectively). It is observed that with increase in functionalization the ordering of the pores are affected to some extent, which is quite natural. However, the basic hexagonal ordering of pore is retained more or less in both the samples. Thus, from powder X-ray diffraction patterns, gas adsorption studies and TEM image analyses the existence of mesopores in the samples could be established.

The FT-IR spectra of the samples at various stages of synthesis using both kind of silica support, MCM-41 and SBA-15, have been recorded by ATR technique and the results are given in Fig. s1 and s2, respectively. Both set of samples showed similar kind of characteristic peaks, as expected, since the functional groups introduced are essentially the same on two different  $SiO_2$  matrices which differ only in their pore size (plot a in both the figures). After functionalization with 3-APTES the mesoporous silicates (plot b) show a broad band in

the range of 3600-2850 cm<sup>-1</sup> which can be attributed to the presence of  $-NH_2$  and  $-CH_2$ - groups. For the *tris*(4-formyl phenyl) amine grafted Schiff-base product, new bands appear around 1695 and 1645 cm<sup>-1</sup> (plot c). The band at 1695 cm<sup>-1</sup> may be assigned to the unreacted carbonyl groups of *tris*(4-formyl phenyl) amine and that at 1645 cm<sup>-1</sup> originates due to the formation of azomethine moiety. After another Schiff base condensation with 2-aminothiophenol (plot d), the band for the carbonyl groups disappear completely indicating conversion of all – CHO to -C=N. Finally, after palladium acetate binds with the solid supports, the bands for azomethine groups shift to somewhat lower wavenumber region (*ca*. 1620 cm<sup>-1</sup>) indicating the participation of the azomethine bond in complexation.



**Fig. 7.** Solid state <sup>13</sup>C CP-MAS NMR spectra of (a) 3-APTES functionalized MCM-41, (b) *tris*(4-formyl phenyl) amine loaded MCM-41, (c) 2-aminothiophenol grafted *tris*(4-formyl phenyl) amine MCM-41 and (d) **MCM-Pd** 

Solid state MAS NMR studies often provide valuable information about the structure of new materials formed, incorporation of organic moieties and metal binding. As established from FT-IR spectra that for both type of SiO<sub>2</sub> frameworks the functional groups introduced in the silica matrices at each step of functionalization are same, the MAS NMR spectra of only MCM-41 based samples have been carried out. The <sup>13</sup>C CP MAS NMR spectra of all the samples except MCM-41 (which does not have any carbon containing counterpart) are shown in Fig. 7. The spectrum of 3-aminopropyl triethoxy silane grafted silica shows peaks at 8.0, 19.7 and 40.4 ppm (Fig. 7a) that can be attributed to the aliphatic carbons of the aminopropyl units. In the *tris*(4-formyl phenyl) amine grafted sample (Fig. 7b) peaks are observed at 10.3, 21.9, 42.3, 61.5, 73.7, 95.1, 96.4, 121.7, 125.8, 127.4, 130.7, 164.8 and 180.4 ppm which indicate the presence of aliphatic and aromatic carbons. This confirms that Schiffbase reaction has occurred between the amine group of the amino propyl moiety and the aldehyde of *tris*(4-formyl phenyl) amine. In Fig. 7c and 7d, the spectra after condensation of residual –CHO groups with 2-aminothiophenol

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and **MCM-Pd** are shown. These are more or less similar to the previous spectrum with identical number of peaks for carbon atoms and small chemical shifts confirming retention of the heterogeneous support after condensation and complex formation.



**Fig. 8.** Solid state <sup>29</sup>Si MAS NMR spectra of (a) calcined MCM-41, (b) 3-APTES functionalized MCM-41, (c) *tris*(4-formyl phenyl) amine loaded MCM-41, (d) 2-aminothiophenol grafted *tris*(4-formyl phenyl) amine MCM-41 and (e) **MCM-Pd** 

To establish the chemical environment around the silicon atom in the samples <sup>29</sup>Si MAS NMR studies of the materials are performed and the results are given in Fig. 8. For the calcined MCM-41, peaks are observed at *ca.* –112.0 and –103.0 ppm (Fig. 8a) which can be ascribed to the Q<sup>4</sup> and Q<sup>3</sup> silica centers of the Si(OSi)<sub>n</sub>(OH)<sub>4-n</sub> units. For the APTES functionalized silica (Fig. 8b), apart from the Q<sup>4</sup> and Q<sup>3</sup> silica species additional peaks appear at –69.0 and –58.3 ppm due to incorporation of the aminopropyl groups. There are literature reports which show that similar kind of hybrid mesoporous silica shows chemical shifts at *ca.* 67 and 58 ppm. These peaks have been attributed to the T<sup>3</sup> ((SiO)<sub>3</sub>Si-R-Si(OSi)<sub>3</sub>) and T<sup>2</sup> ((HO)<sub>2</sub>(OSi)Si-R-Si(OSi)<sub>2</sub>(OH)) species,<sup>67,68</sup> respectively. The spectra for the other two samples, both containing Schiff-base grafted complexes, and the Pd-loaded catalyst, **MCM-Pd** (Fig. 8c-e) are similar to the APTES grafted sample, indicating the formation of imine bond and its retention after metal coordination in the catalyst.

Thermogravimetric analysis has been carried out for calcined mesoporous silica, 3-APTES functionalized silica and *tris*(4-formyl phenyl) amine loaded silica to determine stability of the frameworks and the organic content incorporated into silica support due to functionalization. The study has been carried out from room

temperature to 1200 K and the results for the MCM and SBA series of samples are given in supporting information, Fig. s3 and s4, respectively. From the plots, the amount of APTES and *tris*(4-formyl phenyl) amine loaded on the frameworks are calculated. They are found to be *ca*. 6.12 and 1.11 wt.% (0.66 and 0.11 mmol/g) for the MCM supported samples and 6.56 and 1.66 wt.% (0.63 and 0.17 mmol/g) for the SBA supported samples. The contents of palladium in **MCM-Pd** and **SBA-Pd** has been estimated by ICP-AES analysis and the amounts have been found to be 3.8 mg/g (0.0356 mmol/g) and 4.2 mg/g (0.0393 mmol/g), respectively.

### Catalysis

The catalytic property of **MCM-Pd** and **SBA-Pd** in Suzuki coupling reactions has been studied using various substrates under ambient conditions. At first, the reaction conditions are optimized by tuning various parameters. The coupling reactions are carried out for different reaction times in presence of 10 mg of the catalyst with 1.0 mmol of iodobenzene, 1.2 mmol of phenylboronic acid and 2.5 mmol of base using different solvents and bases which give biaryl derivatives as the products.<sup>69-71</sup> The molar ratio of catalyst/iodobenzene for **MCM-Pd** and **SBA-Pd** is 1.09/1000 and 1.659/1000, respectively, calculated with respect to active Pd-center. To select the most suitable solvent, the first optimization is carried out using different solvents, namely, DMF, CH<sub>3</sub>CN, C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>OH. The reactions are carried out at room temperature using K<sub>2</sub>CO<sub>3</sub> as the base for 24 h and the results are given in Table 2.

### Table 2. Suzuki coupling reactions in different solvents

+ OH	Catalyst, <b>Solvent</b> ►	
∖/ Он	24 h, R.T., K <sub>2</sub> CO <sub>3</sub>	

Entry	Solvent	Time (h)	Yield* (Isolated Yield**) in %	
			MCM-Pd	SBA-Pd
1.	DMF	24	34	52
2.	CH <sub>3</sub> CN	24	45	58
3.	C <sub>2</sub> H <sub>5</sub> OH	24	67	91
4.	CH <sub>3</sub> OH	24	74 (69)	94 (90)

\*Obtained from gas chromatography, \*\*Purified products characterized by <sup>1</sup>H NMR spectroscopy

It is evident that relatively poor yield is obtained when DMF is the solvent (Table 2, entry 1) and the yield increases only marginally in case of acetonitrile (Table 2, entry 2). The yields are best in alcoholic solvents *viz*.  $C_2H_5OH$  and  $CH_3OH$  (Table 2, entries 3 and 4, respectively). For the catalytic reactions aqueous medium is not used as silica framework is susceptible to hydrolysis on prolonged exposure to water under the coupling conditions. However, modification of the silica framework with several organic groups somewhat increases its hydrophobicity and enhances its ability to act as a heterogeneous catalyst in polar alcoholic solvents. Thus, from the above studies,  $CH_3OH$  has been selected as the solvent for all other reactions.

Suzuki coupling reactions are generally carried out in basic medium where the base acts as a co-catalyst for the reaction. It not only neutralizes the acidic by-products of the reaction, it also contributes to increasing the reactivity of the catalyst. For optimizing the conditions, different bases have been used and the reactions are carried out at room temperature in CH<sub>3</sub>OH medium for 24 h. The results have been shown in Table 3. The reactivity is found to decrease in the following order:  $Cs_2CO_3 > K_2CO_3 > NaOH > Na_2CO_3 > NaHCO_3 > Li_2CO_3$ . Since  $K_2CO_3$  is more economic, it is preferred as the base to carry out further studies though it gives slightly lower yield in comparison to  $Cs_2CO_3$ .

OH Catalyst, MeOH OH 24 h, R.T., <b>Base</b>							
Entry	Base	Time (h)	Yield* (Isolated Yield**) in %				
			MCM-Pd	SBA-Pd			
1.	Li <sub>2</sub> CO <sub>3</sub>	24	67	84			
2.	Na <sub>2</sub> CO <sub>3</sub>	24	71	88			
3.	K <sub>2</sub> CO <sub>3</sub>	24	74	94			
4.	$Cs_2CO_3$	24	76	94.5			
5.	NaHCO <sub>3</sub>	24	67	87			
6.	NaOH	24	72	90			

\*Obtained from gas chromatography, \*\*Purified products characterized by <sup>1</sup>H NMR spectroscopy

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Time and temperature are other two very important parameters for these reactions. At first, the coupling reactions are carried out at room temperature for different time periods (Table 4, entries 1-5). As expected, with increase in time the yield of biphenyl product gradually increases for both the catalysts. It has been observed that the yield for **MCM-Pd** always remains less than **SBA-Pd** and even after 72 h of reaction the yield reaches only up to 81 %. However, for **SBA-Pd** the yield is found to be 94% within 24 h of the reaction. Hence all the reactions have been carried out for 24 h. Regarding the temperature, it is expected that the rate of a reaction will increase with the increase in temperature. It is nothing but providing energy externally in the form of heat to enhance the rate of the reaction. Thus, for both the catalyst it has been found that at elevated temperature (333 K) the conversions are reasonably high within 6-12 h (Table 4, entries 6 and 7). The yields for **MCM-Pd** and **SBA-Pd** reach to 96 and 99 %, respectively, in 12 h. However, the objective of this study is to see the effect of pore dimension on the reactivity of the catalysts and hence the results obtained at ambient temperature have been considered for the purpose of comparison.

Table 4. Suzuki coupling reactions at different time and temperature

OH

$ \begin{array}{c c} & & & \\ & & & \\ & & $						
Entry	Time (h)	Temperature (K)	Yield* (Isolated	Yield* (Isolated Yield**) in %		
			MCM-Pd	SBA-Pd		
1.	12	300 K	56	72		
2.	24	300 K	74 (69)	94 (90)		
3.	36	300 K	75	95		
4.	48	300 K	78	97		
5.	72	300 K	81	98		
6.	6	333 K	72	90		
7.	12	333 K	96	> 99		

Catalyst, MeOH

\*Obtained from gas chromatography, \*\*Purified products characterized by <sup>1</sup>H NMR spectroscopy

After the optimization studies, Suzuki coupling reactions are carried out between various bromo-/iododerivatives and phenylboronic acid in CH<sub>3</sub>OH medium using K<sub>2</sub>CO<sub>3</sub> as the base at room temperature for 24 h. For the comparative study, apart from bromo- and iodo-benzene, other electron-withdrawing and electron-donating substrates have also been used and the results are shown in Table 5. It is found that the yield of the biaryl derivatives vary depending on the catalyst used. The corresponding TOF values for each entry are also calculated and given in the table.

Table 5. Suzuki coupling reactions over different substrates under optimized reaction condition

		ОН	Catalyst, MeOH	
R	+	ОН	24 h, R.T., K <sub>2</sub> CO <sub>3</sub>	\_ =∕ R

Entry	R	X	Time	Yield* (Isolated Yield**) in %		<b>TOF</b> ***	
			(h)	MCM-Pd	SBA-Pd	MCM-Pd	SBA-Pd
1.	Н	Br	24	50	78 (74)	60	82
2.	Н	Ι	24	74 (69)	94 (90)	88	99
3.	4CH3	Br	24	72	90 (85)	85	93
4.	4-CH <sub>3</sub>	Ι	24	81	93 (89)	96	98
5.	2-CH3	Br	24	84	93 (88)	100	98
6.	4–OCH <sub>3</sub>	Br	24	73	90 (84)	86	93
7.	4–OCH <sub>3</sub>	Ι	24	75	93 (88)	88	98
8.	4–Cl	Br	24	68	88 (81)	80	93
9.	4–COCH <sub>3</sub>	Br	24	78	94 (89)	92	99
10.	4–COCH <sub>3</sub>	Ι	24	85	98 (94)	100	104
11.	$4-NO_2$	Br	24	65	92 (87)	78	97
12.	$4-NO_2$	Ι	24	66	94 (90)	77	99
13.	4-соон	Br	24	69	92 (86)	81	97
14.	4-соон	Ι	24	70	96 (91)	82	101

\*Obtained from gas chromatography, \*\*Purified products characterized by <sup>1</sup>H NMR spectroscopy, \*\*\*TOF: turnover frequency (moles of substrate converted per mole of metal center per hour)

The <sup>1</sup>H NMR spectra and data<sup>72</sup> of the purified samples have been given in the supporting information.

The conversion of bromobenzene is considerably less in comparison to iodobenzene and in all the cases it is seen that the iodo-derivative is more reactive. For all the substrates, the yield of product with **MCM-Pd** is found to be significantly lower than **SBA-Pd**. For both the catalysts the conversion of electron-donating substituents (Table 5, entries 3-8) is lower compared to those with electron-withdrawing substituents (Table 5, entries 9-14). The possible explanation for the observations in Table 5 has been given later.

### Recyclability and test for heterogeneity

Heterogeneous catalysts are advantageous because they are recyclable. In order to study the recyclability of **MCM-Pd** and **SBA-Pd**, the catalysts have been recovered after each reaction cycle, regenerated and used in subsequent cycles under identical conditions. Fig. 9 shows the plot of conversion (%) against the number of reaction cycles for both the catalysts for the coupling reaction of iodobenzene with phenylboronic acid in the presence of K<sub>2</sub>CO<sub>3</sub> for 24 h at ambient temperature. Three successive reaction cycles have been performed and it can be seen that there isn't any substantial loss of activity for any of the catalysts after the repeated reactions. The TEM image of **SBA-Pd** after three reaction cycles has been given in supporting information, Figure s5. It can be seen that the porous structure is retained and also there is no formation of Pd-nanoparticles. The color of the catalysts after the reactions does not blacken which also indicate that metal nanoparticles are not involved in the catalytic cycle. These results suggest that both **MCM-Pd** and **SBA-Pd** preserve their characteristic properties after the reaction cycles and hence function as recyclable catalysts. Since the aim of this work is to study the effect of pore dimension of the solid catalyst support on the reactivity, reactions are not conducted further after the third cycle.



Fig. 9. Recycling efficiency of MCM-Pd and SBA-Pd for Suzuki coupling of iodobenzene and phenylboronic acid under ambient temperature

To confirm the heterogeneity of **MCM-Pd** and **SBA-Pd**, coupling reactions of iodobenzene have been carried out with phenylboronic acid under optimized condition and after 4 h of the reactions the catalysts are removed from the reaction mixtures. After that the reactions are continued for the usual reaction time of 24 h. For both the catalysts, it is found that after separation from the reaction medium no increase in conversion takes place. This suggests that the reactions proceed only in the presence of the heterogeneous solid catalysts. In addition to this, the reaction mixtures collected by filtration are analyzed by ICP-AES and it is found that the palladium contents are below detection limit. The results confirm that palladium is not leached out from the solid support into the reaction mixture and the catalyst is truly heterogeneous in nature where the active palladium species is bound strongly by covalent bond to the functionalized silica support.

### Mechanism and effect of pore size

In the present work we are studying two catalytic systems, **MCM-Pd** and **SBA-Pd**, which are different from each other with respect to the solid support used. For **MCM-Pd**, the silica support MCM-41 is synthesized with CTAB template and the average size of the pores is 3.8 nm (Fig. 5). On the other hand, for **SBA-Pd** Pluronic P123 is used as template which gives rise to bigger pore sizes with an average of 7.6 nm (Fig. 5). The pore sizes are dependent on the dimension of the self-assemblies formed by the template molecules. In both the catalysts, palladium is coordinated to the N and S atoms of the Schiff-base and thiol group of 2-aminothiol, respectively, which are immobilized over the mesoporous silica supports. It is interesting to note that the first Schiff base condensation of *tris*(4-formyl phenyl) amine with the amino-group of APTES introduces two more aldehyde groups into the framework. These two aldehydes in the next step of Schiff base condensation with 2-aminothiol give two N,S-donor sites which can bind to two palladium centers of palladium acetate. Thus, two successive steps of Schiff base condensation increase the number of active sites capable of binding the metal ion in the catalysts. The most preferred geometry for palladium is square planar and the other two coordination sites are fulfilled by two acetate ions (OAc<sup>-</sup>) from the metal precursor Pd(OAc)<sub>2</sub>. The oxidation state of Pd is +II in the precatalyst, <sup>73, 74</sup> from which Pd(0) is formed *in situ* in the reaction mixture in presence of phenyl boronic acid and the base. A brief mechanism of Suzuki coupling reaction is given in supporting information, Fig. s6.

For both MCM-Pd and SBA-Pd the steps involved in the coupling reaction are essentially the same. So the difference in reactivity must be arising from some other aspect. It is known that all reactions take place at the surface. Greater the surface available more will be the reactivity of a catalyst. Now for MCM-41 based catalyst, MCM-Pd the size of the pore is smaller compared to the SBA-15 based catalyst, SBA-Pd. Thus, the surface exposure available for the former is lesser compared to the latter. Apart from that, greater pore space is available for SBA-Pd which allows substrates to comfortably diffuse inside the pores and come in contact with the active sites on the surface of the catalyst. Thus both the availability of more active sites on catalyst surface as well as bigger size of the pores contributes to the higher reactivity of SBA-Pd than MCM-Pd. However, this result is

only true when the catalysis is carried out at room temperature when no activation energy is supplied externally. However, when the reactions are carried out at 333 K, it is found that **MCM-Pd** behaves as a very good catalyst. Also there are ample examples of MCM-41 based Pd-materials as very effective catalysts in Suzuki Coupling reactions at higher temperature.<sup>17,67</sup> This result indicates that the mesopores in MCM-type of materials are also superior compared to bulk or microporous catalysts<sup>68</sup> but the reactivity can be better with bigger mesopores. That is the reason why **SBA-Pd** derived from a solid support with bigger pore size shows very high reactivity even under ambient conditions. On the other hand, for **MCM-Pd** elevated temperature *i.e.* supply of external energy is required to attain the same extent of reactivity.

Now coming to the reactivity of various substrates in the Suzuki coupling reactions, the oxidative addition step must be considered. In most cases this is the rate determining step in the Tolman's cycle where an aryl halide gets inserted into the palladium center to give an organo-palladium species. As a result of this Pd(0) is oxidized to Pd(II). This step involves the carbon-halogen bond breaking and palladium binds to the halogen as well as the Ar group. Now, if there is any electron-withdrawing group present in the *para* position of the aryl halide (with respect to halide), the carbon-halogen bond cleavage becomes more facile. Thus, the reactivity of these substrates increase compared to those with an electron-donating group at the *para* position. This explains the results that are obtained and given in Table 5 where the electron-withdrawing substituents, -COCH<sub>3</sub>, -NO<sub>2</sub> and -COOH give higher yield than electron-donating substitutions, -CH<sub>3</sub>, -OCH<sub>3</sub> and -Cl.

### Conclusions

In the present article, we report two different Pd-catalysts, **MCM-Pd** and **SBA-Pd** based on two different types of silica supports with different pore sizes. The silica supports are functionalized taking advantage of the aminopropyl groups grafted into the framework and subjected to two steps of Schiff base condensation to introduce two N,S-donor sites which can bind to Pd-centers. The materials at different stage are characterized for their microstructure, porosity, functionalization and metal binding. Both the catalysts can heterogeneously catalyze Suzuki coupling reactions of a range of substrates, which includes both electron-donating and electron-withdrawing ones, but to different extents. The catalyst based on a smaller mesopore is less reactive compared to the higher pore-size counterpart when the reactions are carried out under ambient conditions. However, the reactivity of both the catalysts is leveled at high temperature where energy is supplied externally. This indicates that bigger pore dimension of the heterogeneous support facilitates the catalytic reactions. This can be attributed to both the availability of higher pore wall surface exposed for the reactions as well as the ease of accessibility of the substrates inside the pocket of the pores. This is a rare example of systematic study of heterogeneous Suzuki coupling reaction where the effect of pore size of the solid catalyst support has been studied.

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### References

- [1] N. Miyaura and A. Suzuki, Chem. Rev., 1995, 95, 2457.
- [2] N. Miyaura and A. Suzuki, Chem. Comm., 1979, 19, 866.
- [3] K. C. Nicolaou, P. G. Bulger and D. Sarlah, Angew. Chem., Int. Ed., 2005, 44, 4442.
- [4] Á. Molnár, Chem. Rev., 2011, 111, 2251.
- [5] A. Fihri, M. Bouhrara, B. Nekoueishahraki, J. M. Basset and V. Polshettiwar, *Chem. Soc. Rev.*, 2011, 40, 5181.
- [6] J. P. Wolfe, R. A. Singer, B. H. Yang and S. L. Buchwald, J. Am. Chem. Soc., 1999, 121, 9550.
- [7] R. Garrido, P. S. H. Montes, Á. Gordillo, P. G. Sal, C. L. Mardomingo and E. de Jesús, *Organometallics*, 2015, 34, 1855.
- [8] Y. Ma, X. Ma, Q. Wang and J. Zhou, *Catal. Sci. Technol.*, 2012, **2**, 1879.
- [9] N. T. S. Phan, M. V. D. Sluys and C. W. Jones, Adv. Synth. Catal., 2006, 348, 609.
- [10] A. Corma, D. Das, H. García and A. Leyva, J. Catal., 2005, 229, 322.
- [11] A. Corma and H. Garcia, *Chem. Rev.*, 2002, **102**, 3837.
- [12] M. Poliakoff, J.M. Fitzpatrick, T.R. Farren and P.T. Anastas, Science, 2002, 297, 807.
- [13] S. M. Sarkar, Md. L. Rahman and M. M. Yusoff, New J. Chem., 2015, 39, 3564.
- [14] X. Feng, M. Yan, T. Zhang, Y. Liu and Ming Bao, Green Chem., 2010, 12, 1758.
- [15] J. Čejka, R. E. Morris and D. P. Serrano, *Catal. Sci. Technol.*, 2016, 6, 2465.
- [16] A. Gniewek, J. J. Ziółkowski, A. M. Trzeciak, M. Zawadzkib, H. Grabowska and J. Wrzyszcz, J. Catal., 2008, 254, 121.
- [17] J. P. V. Damasceno, C. M. Maroneze, M. Strauss, F. A. Sigoli and I. O. Mazali, New J. Chem., 2016, 40, 6636.
- [18] L. Shang, T. Bian, B. Zhang, D. Zhang, L.-Z. Wu, C.-H. Tung, Y. Yin and T. Zhang, Angew. Chem., Int. Ed., 2014, 53, 250.
- [19] K. Sarkar, M. Nandi, M. Islam, M. Mubarak and A. Bhaumik, Appl. Catal. A Gen., 2009, 352, 81.
- [20] L. C. Lee, J. He, J. Q. Yu and C. W. Jones, ACS Catal., 2016, 6, 5245.
- [21] M. Nandi and H. Uyama, RSC Adv., 2014, 4, 20847.
- [22] K.C. Gupta, A. K. Sutar and C. C. Lin, Coord. Chem. Rev., 2009, 253, 1926.
- [23] X. Xu, Y. Li, Y. Gong, P. Zhang, H. Li, Y. Wang, J. Am. Chem. Soc., 2012, 134, 16987.
- [24] X. Wang, S. Wu, Z. Li, X. Yang, H. Su, J. Hu, Q. Huo, J. Guan and Q. Kan, *Microporous Mesoporous Mater.*, 2016, 221, 58.
- [25] H. Yu, K. Zeng, X. Fu, Y. Zhang, F. Peng, H. Wang and J. Yang, J. Phys. Chem. C, 2008, 112, 11875.
- [26] M. Bazarganipour and M. S. Niasari, Appl. Catal. A, 2015, 502, 57.
- [27] A. Zarnegaryan, M. Moghadam, S. Tangestaninejad, V. Mirkhani and I. M. Baltork, New J. Chem., 2016,

40, 2280.

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- [28] M.-R. Gao, X. Cao, Q. Gao, Y.-F. Xu, Y.-R. Zheng, J. Jiang and S.-H. Yu, ACS Nano, 2014, 8, 3970.
- [29] H. Noh, Y. Cui, A. W. Peters, D. R. Pahls, M. A. Ortuñ, N. A. Vermeulen, C. J. Cramer, L. Gagliardi, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2016, **138**, 14720.
- [30] T. Toyao, K. Miyahara, M. Fujiwaki, T.-H. Kim, S. Dohshi, Y. Horiuchi and M. Matsuoka, J. Phys. Chem. C, 2015, 119, 8131.
- [31] H. S. Oh, H. N. Nong, T. Reier, A. Bergmann, M. Gliech, J. F. D. Araújo, E. Willinger, R. Schlögl, D. Teschner and P. Strasser, J. Am. Chem. Soc., 2016, 138, 12552.
- [32] D. Dehe, L. Wang, M. K. Müller, G. Dörr, Z. Zhou, R. N. K. Taylor, Y. Sun, S. Ernst, M. Hartmann, M. Bauer and W. R. Thiel, *ChemCatChem*, 2015, 7, 127.
- [33] C. Kim, H. S. Jeon, T. Eom, M. S. Jee, H. Kim, C. M. Friend, B. K. Min and Y. J. Hwang, J. Am. Chem. Soc., 2015, 137, 13844.
- [34] Y. Li, F. Mao, T. Chen, Z. Zhou, Y. Wang and J. Huang, Adv. Synth. Catal., 2015, 357, 2827.
- [35] C. M. A. Parlett, K. Wilson and A. F. Lee, Chem. Soc. Rev., 2013, 42, 3876.
- [36] L. Yin and J. Liebscher, Chem. Rev., 2007, 107, 133.
- [37] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, 359, 710.
- [38] F. Pereira, K. Valle, P. Belleville, A. Morin, S. Lambert and C. Sanchez, Chem. Mater., 2008, 20, 1710.
- [39] A. Corma and H. Garcia, Adv. Synth. Catal., 2006, 348, 1391.
- [40] D. H. Lee and M. J. Jin, Org. Lett., 2011, 13, 252.
- [41] A. F. Littke and G. C. Fu, Angew. Chem., Int. Ed., 2002, 41, 4176.
- [42] A. C. Frisch and M. Beller, Angew. Chem., Int. Ed., 2005, 44, 674.
- [43] T. B. Halima, W. Zhang, I. Yalaoui, X. Hong, Y. F. Yang, K. N. Houk and S. G. Newman, J. Am. Chem. Soc., 2017, 139, 1311.
- [44] A. J. J. Lennox and G. C. L. Jones, Chem. Soc. Rev., 2014, 43, 412.
- [45] T. Das, H. Uyama and M. Nandi, J. Solid State Chem., https://doi.org/10.1016/j.jssc.2018.01.027.
- [46] A. Kumar, G. K. Rao, S. Kumar and A. K. Singh, *Dalton Trans.*, 2013, 42, 5200.
- [47] P. P. Mpungose, N. I. Sehloko, G. E. Maguire and H. B. Friedrich, New J. Chem., 2017, 41, 13560.
- [48] D. V. Jawale, E. Gravel, C. Boudet, N. Shah, V. Geertsen, H. Li, I. N. N. Namboothiri and E. Doris, *Catal. Sci. Technol.*, 2015, 5, 2388.
- [49] Z. Zhou, Z. Zhou, A. Chen, X. Zhou, Q, Qi, Y. Xie, Transition Met. Chem., 2013, 38, 401.
- [50] I. Hoffmann, B. Blumenröder, S. O. Thumann, S. Dommer and J. Schatz, Green Chem., 2015, 17, 3844.
- [51] A. F. Asachenko, K. R. Sorochkina, P. B. Dzhevakov, M. A. Topchiy and M. S. Nechaev, Adv. Synth. Catal., 2013, 355, 3553.
- [52] A. G.-Choghamarani and M. Norouzi, New J. Chem., 2016, 40, 6299.

- [53] T. E. Barder, S. D. Walker, J. R. Martinelli and S. L. Buchwald, J. Am. Chem. Soc., 2005, 127, 4685.
- [54] R. B. Bedford, C. S. J. Cazin and S. L. Hazelwood, Angew. Chem., Int. Ed., 2002, 41, 4120.
- [55] D. Chandra, N. K. Mal, M. Mukherjee and A. Bhaumik, Ind. Eng. Chem. Res., 2006, 45, 4879.
- [56] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. Fredrickson, B. Chmelka and G.D. Stucky, *Science*, 1998, 279, 548.
- [57] C. M. Crudden, M. Sateesh and R. Lewis, J. Am. Chem. Soc., 2005, 127, 10045.
- [58] T. Kang, Y. Park and J. Yi, Ind. Eng. Chem. Res., 2004, 43, 1478.
- [59] T. Das, A. Roy, H. Uyama, P. Roy and M. Nandi, *Dalton Trans.*, 2017, 46, 7317.
- [60] T. Mallegol, S. Gmouh, M. A. A. Meziane, M. B.-Desce and O. Mongin, Synthesis, 2005, 11, 1771.
- [61] A. P. Wight and M. E. Davis, Chem. Rev., 2002, 102, 3589.
- [62] A. Stein, Adv. Mater., 2003, 15, 763.
- [63] S. Inagaki, Y. Fukushima and K. J. Kuroda, J. Chem. Soc., Chem. Commun., 1993, 680.
- [64] P. T. Tanev, M. Chibwe and T. J. Pinnavaia, *Nature*, 1994, 368, 321.
- [65] P. T. Tanev and T. J. Pinnavaia, Science, 1996, 271, 1267.
- [66] D. Zhao, J. Sun, Q. Li and G. D. Stucky, Chem. Mater., 2000, 12, 275.
- [67] S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna and O. Terasaki, J. Am. Chem. Soc., 1999, 121, 9611.
- [68] S. Inagaki, S. Guan, T. Ohsuna and O. Terasaki, Nature, 2002, 416, 304.
- [69] B. D. Briggs, R. T. Pekarek and M. R. Knecht, J. Phys. Chem. C, 2014, 118, 18543.
- [70] S. Tanaka, T. Kaneko, N. Asao, Y. Yamamoto, M. Chen, W. Zhang and A. Inoue, *Chem. Commun.*, 2011, 47, 5985.
- [71] Y. Jang, J. Chung, S. Kim, S. W. Jun, B. H. Kim, D. W. Lee, B. M.Kim and T. Hyeon, *Phys. Chem. Chem. Phys.*, 2011, 13, 2512.
- [72] L. Liu, Y. Zhang and Y. Wang, J. Org. Chem., 2005, 70, 6122.
- [73] Y. Yu, T. Hu, X. Chen, K. Xu, J. Zhang and J. Huang, Chem. Commun., 2011, 47, 3592.
- [74] K. Dhara, K. Sarkar, D. Srimani, S.K. Saha, P. Chattopadhyay and A. Bhaumik, *Dalton Trans.*, 2010, 39, 6395.
- [75] D. E. De Vos, M. Dams, B. F. Sels and P. A. Jacobs, Chem. Rev., 2002, 102, 3615.

### **Table of Content**



Pronounced effect of pore dimension of silica support on Pd-catalyzed Suzuki coupling reaction under ambient conditions

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The pore size of mesoporous silica support affects the reactivity of heterogeneous Palladium catalysts in Suzuki reaction under ambient conditions which is leveled at higher temperature.