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# ARTICLE TYPE

### Mesoporous silica polymer nanocomposites encapsulated with polyphosphoric acid for synthesis of β-amino carbonyl compounds under environmental benign conditions

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Mesoporous silica-polymer nanocomposites (SBA/PS) synthesized via wet impregnation method was functionalized by mild polyphosphoric acid (PPA) for catalytic application. The catalysts were characterized and analysed by Powder X-ray Diffraction (PXRD), Solid State Nuclear Magnetic

<sup>10</sup> Resonance (<sup>31</sup>P-SSNMR), N<sub>2</sub>-Adsorption-Desorption Isotherm, Fourier Transform-Infrared (FT-IR), Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (HR-TEM) and Thermogravimetric Analysis (TGA/DTA). The catalytic studies of a multicomponent Mannich reaction was conducted wherein the hydrophobic nature of these nanocomposites showed an enhancement in the product activity and selectivity of  $\beta$ -amino carbonyl (Mannich base) compounds. Probable reaction

15 mechanism elucidates the role of well distributed active sites on the hydrophobic surface and the stability of the catalyst for good catalytic activity.

#### Introduction

The discovery of mesoporous materials have gained tremendous interest since it acts as an excellent medium for embedding 20 polymers; especially ordered mesoporous silica (OMS) materials are an ideal tethering agent for entrapping the polymers at the surface strongly<sup>1</sup>. The flexible pore architecture and high surface area of OMS allows fabrication of organic-inorganic nanocomposites with different polymer functionalities for desired 25 applications. This penetrating network of polymer inside the

- silica improves the flexibility, mechanical strength and generates modulation in controlling the degree of hydrophilicity/hydrophobicity on the surface property. Such properties are essential for tuning and transforming these
- 30 nanocomposites into a highly efficient catalyst. Though many researchers have already incorporated the polymers directly on the surface of silica however in most of the cases the structural order either collapsed completely or became almost nonporous. Therefore methods were devised for uniform distribution of
- 35 polymer over the inner pore surface while retaining the mesoporosity and enhancing the active surface area<sup>2</sup>. This enables the synthesized nano-catalyst to exhibit better stability, uniformity and strength with an appropriate spatial distribution.
- In recent years, heterogeneous catalysts have been introduced 40 to address the sustainability issues and have emerged as an alternative approach for limiting the homogeneous acid catalyst which are often highly toxic, environmentally hazardous, and corrosive and produce lot of wastes<sup>3</sup>. Particularly, the introduction of controlled hydrophobicity on highly hydrophilic
- 45 silica surface could be interesting for achieving higher selectivity

for catalytic applications. Therefore, in order to synthesize stable nano-catalyst effectively, the catalytic active moieties are dispersed in the embedded polymer matrix to form one of the structural components of the framework<sup>4</sup>. Furthermore, the 50 catalytic moieties can be incorporated inside the framework by cross linking the monomers to the silica surface directly via impregnation or grafting method for their subsequent controlled radical polymerization<sup>5-6</sup>. This provides uniform functional density of the monomers on the surface of the silica framework 55 for catalytic, sensors, ion exchange and adsorption applications. Multicomponent reaction has emerged as a proficient, one-pot synthesis of complex-organic molecules from readily available substrates without isolating any intermediate; this reduces time and energy as compared to the conventional reaction procedures  $_{60}$  <sup>7-9</sup>. Various biologically active compounds especially  $\beta$ -amino carbonyl compounds act as a precursor for antibacterial<sup>10</sup>, antitumor, anticancer, anti-inflammatory drugs<sup>11-13</sup>; for which amino alcohols, peptides, lactams, optically active amino acids respectively have been synthesized via Mannich reactions. So far 65 several catalysts such as ionic liquid<sup>14</sup>, Cu-nanoparticles<sup>15</sup>, SnTUD1 nanoparticles<sup>16</sup>, phosphonic acids<sup>17</sup>, metal salts, heteropoly acids<sup>18</sup>, polyaniline<sup>19</sup>, Si-Al<sub>2</sub>O<sub>3</sub><sup>18</sup> have been employed for Mannich reaction but silica polymer nanocomposites functionalized with polyphosphoric acid (PPA), a mild catalyst 70 have not been employed yet. Moreover the present catalyst has a greener role to play since it can overcome the constraints related to the need of strong acidic sites in many selective catalytic reactions. Recently, we have reported the acylation of naphthalene over SBA-Polyphosphoric acid (SBA/PPA) 75 nanocomposites in liquid phase with very high selectivity of 2acetylnaphthalene<sup>20</sup>. In the present studies, efforts are devoted to

modify the surface properties via in-situ polymerization of vinyl monomers followed by incorporation of PPA. The endeavor of incorporating vinyl monomers is to enhance the degree of hydrophobicity on the highly hydrophilic silica surface for varied 5 structural properties particularly for higher selectivity in organic transformations and PPA was chosen because of its mild acidic behavior (pKa= 2.1). Moreover devising such ways for a multicomponent reaction (MCR) in an environmentally benign way would result in enhanced and improved atom economy.

#### 10 Experimental

#### Synthesis of SBA-15

All the chemicals were procured from Sigma-Aldrich and used without further purification. The synthesis of SBA-15 is carried out using Pluronic (P123) (EO20PO70EO20,MW = 5800, 15 Aldrich) as the surfactant and tetra ethoxy ortho-silicate (TEOS) as a silica source, respectively<sup>21</sup>. In a typical synthesis batch with TEOS, 3 g of P123 was dissolved in 100 g of distilled water and 5.9 g of conc. HCl (35%). After stirring for 1 h, 7.3 g of TEOS (ACROS, 98%) was added at 35°C while maintaining the molar 20 ratio of P123: H<sub>2</sub>O: HCI: TEOS ratio as 1: 5562.9: 86.29: 42.51 and continued stirring for 24 h. Subsequently the mixture was heated for 24 h at 100°C under static conditions in a closed polypropylene bottle. The solid product obtained after the hydrothermal treatment was filtered and dried at 80°C. The 25 template was removed by calcinations at 550°C for 6 h.

#### Synthesis of PPA functionalized silica polymer nanocomposite (SBA/PS/PPA)

The synthesis methodology of polymer supported silica (SBA/PS) involves the incorporation of vinyl monomers (styrene 30 and divinyl benzene), cross linkers and radical initiators into the SBA-15 mesopore walls via the wet-impregnation method <sup>6</sup> and equilibrated under reduced pressure to achieve a uniform distribution. The monomers adsorbed on the mesopore walls were subsequently polymerised with temperature programmed heating.

- 35 Typically, for 30 wt% polymer loading of polymer on SBA-15, 0.114 g of styrene (80 mol%), 0.0358 g divinylbenzene (20 mol%), 0.0065 g of AIBN, a,a9-azoisobutyronitrile (3% relative to the total vinyl group) were dissolved into 2 ml of solvent (dichloromethane). The resulting mixture was impregnated
- 40 uniformly into the SBA-15 framework. After impregnating the solution, the sample was heated to 40°C to remove the dichlorobenzene and subjected to freeze-vacuum-thaw to remove the residual solvent and air. The sample was subjected to controlled temperature programming for polymerization. The 45 temperature scheme follows 45°C for 24 h, 60°C for 4 h, 100°C,
- 120°C and 150°C for 1 h. Finally the polymer was washed with ethanol to remove excess of monomers. Samples with 10 and 20 wt% polymer loading were also synthesized under similar conditions and named as SBA/PS. The role of styrene is to make
- 50 the surface more hydrophobic. Different amount (5, 10, 20, 30 wt%) of PPA was incorporated on SBA/PS using ethanol as a solvent. Typically for 20wt% incorporation of PPA, 600mg of PPA in ethanol was impregnated on SBA/PS for 2h at reflux

temperature. The reaction mixture was cooled, filtered and 55 washed with excess solvent to remove the residual PPA and dried at 80°C for 12h. Finally the samples were named as SBA/aPS/xPPA, where a and x represents the wt% of polymer and PPA incorporated respectively. Similarly PPA of (5, 10. 20, 30 wt%,) was impregnated over SBA-15 without surface 60 modification and named as SBA/xPPA (imp) where "imp" stands for impregnation.

#### **Characterization details**

PXRD pattern was recorded on Hecus X-Ray Systems S3 Model using Cu K $\alpha$  radiation (k = 1.5404 A). Nitrogen adsorption-65 desorption isotherms were measured by using Quantachrome NOVA series. Prior to the measurements, the materials were outgassed at 80°C under vacuum for 12 h. The specific surface area was calculated by the BET method and the pore size distribution was calculated from the desorption isotherms by the 70 Barrett-Joyner-Halenda (BJH) method. Solid state NMR <sup>31</sup>P of samples was recorded on AV500S - 500 MHz High Resolution Multinuclear FT-NMR Spectrometer at 121.4 MHz with a 5mm CP/MAS probe and magic spinning frequency of 5 KHz and adenosine triphosphate was chosen as a standard. The IR spectra 75 of samples (as KBr pellets) were recorded using a Schimadzu FTIR spectrophotometer in the range of 400-4000 cm<sup>-1</sup>. The number of acidic sites on the catalyst surface was determined by titration method. Scanning Electron Microscopy was used to confirm the structural morphology of PPA functionalized silica <sup>80</sup> polymer nanocomposites, Energy Dispersive X-ray Analysis (EDX, Oxford INCA250 energy, UK) was also performed. Microstructural characterization was conducted using Tecnai G<sup>2</sup> F30 S-Twin (FEI; Super Twin lens with Cs =1.2 mm) instrument operated at an accelerating voltage at 300 kV, having a point 85 resolution of 0.2nm and lattice resolution of 0.14nm. Program Digital Micrograph (Gatan) was used for image processing. The TEM samples were prepared by drying a droplet of PPA functionalized silica polymer nanocomposites on a carbon grid. Thermogravimetric measurements (TGA) were performed under <sup>90</sup> air atmosphere on equipment Netzch in the temperature range from 30 to 1000°C at 20°C/min. Synthesis of β-amino carbonyl compunds

The catalytic activity studies were carried out for one pot three component reaction between aniline, benzaldehyde and 95 acetophenone to achieve the synthesis of Mannich base under solvent free conditions (Scheme.1). Typically, 1mmol of all the three reactants were taken in round bottom flask under stirring conditions at 52°C without any solvent. After 15 minutes, the catalyst was added into the reaction mixture and the reaction was 100 monitored by TLC for 24hrs. The products of the reaction were isolated and compared with the authentic samples. Finally, the yield of the product was calculated after purification of the product.

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## ARTICLE TYPE



**Scheme1 Mannich Reaction** 

#### **Results and Discussions**

#### Characterization of PPA functionalized silica s polymer nano-composite(SBA/PS/PPA).

#### **PXRD** studies

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Powder X-ray diffraction pattern of the samples (Fig.1) at low angles shows the diffraction pattern similar to SBA-15. The <sup>10</sup> diffraction at (100), (110), and (200) planes can be indexed to reflections comprising of hexagonal p6mm space group <sup>21</sup>indicating that the materials possess an ordered mesoporous structure and polyphosphoric acid has been incorporated inside the framework. A careful examination of the spectrum showed <sup>15</sup> increase in the intensity of the base peak in SBA/30PS/10PPA catalyst compared to the SBA/PPA catalyst due to the polymer formation inside the mesopores of silica materials resulting in an increase in the apparent density of the polymer on the mesopore walls than the pores of the nanocomposite resulting in <sup>20</sup> distinguished scattering contrast. This increased intensity probably gives an indication towards a uniform coating of the

polymer on the mesopore walls<sup>6</sup>.





#### N<sub>2</sub>Adsorption studies

 $N_{\rm 2}$  adsorption isotherms were measured by volumetric adsorption

analyzer and showed a Type IV adsorption isotherm indicating the mesoporous nature of the samples (Fig.2) according to the IUPAC classification<sup>21</sup>. A sharp capillary condensation step at relatively high pressure  $p/p_0= 0.5-0.7$  with an H1 hysteresis loop indicates the presence of large mesopores with narrow pore size distributions. The surface area, pore volume and pore diameter decreased with the incorporation of polymer and PPA indicating that the polymer and PPA has been incorporated inside the SBA framework. Also the structural parameters of only PPA

<sup>40</sup> incorporated SBA-15 (SBA/30PPA) showed variations from polymer coated silica (SBA/PS/PPA) incorporated with PPA as given in Table 1.





#### <sup>13</sup>C CP-MAS NMR

<sup>50</sup> Incorporation of PPA inside the silica framework was further confirmed by <sup>13</sup>C CP-MAS SSNMR. The spectrum of SBA/PS (Fig.3(a)) showed peaks at 128, 139 and 120 ppm indicating the presence of aromatic carbons of the polymer resulted from the monomers styrene and divinyl benzene<sup>22</sup>. The peak at 25 ppm is little upfield showing the presence of the carbon directly

5	5 Table 1 Structural Parameters of functionalized mesoporous	silica
	nanocmposites (SBA/PS/PPA)	

Materials	Surfac	Pore	$a_0^{1}$	h <sub>0</sub> <sup>2</sup> (nm	Por
	e area	Volum	(nm)	)	e
	(m <sup>2</sup> /g)	e			Size
		(cm <sup>3</sup> /g)			<b>(D</b> )
					(nm
					)
SBA-15	678	1.2	10.8	3.4	7.4
SBA/30PPA	391	0.43	10.7	6.0	4.7
SBA/30PS	312	0.59	-	-	4.0
SBA/30PS/30PP	221	0.46	-	-	3.8
Α	221	0.70			5.8
SBA/30PS/10PP	114	0.20	11.0	8.2	2.0
А	114	0.20			2.8

<sup>a</sup> pore size distribution analysis- BJH method

<sup>1</sup> hexagonal unit-cell dimension (a<sub>0</sub>)=  $2d_{100}/\sqrt{3}$ 

 $^{2}$  h<sub>0</sub> wall thickness = a<sub>0</sub>-D

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linked to mesoporous silica (-CH<sub>2</sub>-Si-). However incorporation of PPA inside the silica framework was further identified by <sup>31</sup>P magic angle spinning (MAS) NMR. NMR spectrum of the samples (Fig.3(b)) exhibits two different peaks at -0.3 and -10.85 <sup>15</sup> ppm indicating the distinct nature of phosphorus incorporated inside the silica framework<sup>23</sup>. The peak in the spectra clearly indicates the presence of PPA over the polymeric surface similar

to our previous studies.



The SEM images of SBA/PS/PPA with different polymer and PPA weights are shown in the Fig.4, the rod shaped particles are evenly dispersed with relatively uniform size of  $1 \mu m$ . The

polymer and the impregnated polyphosphoric acid on ordered <sup>25</sup> mesoporous silica material are uniformly dispersed which results in better catalytic activity and selectivity. SEM/EDX was also done which showed the presence of Si, O, C and P in the framework. The average amount of P atoms in SBA/PS matrix was estimated to be about in (0.37%), (0.62%), (0.8%) <sup>30</sup> (atomic wt%) for SBA/30PS/10PPA, SBA/30PS/20PPA, SBA/30PS/30PPA which is in correlation with the theoretical value.

#### HRTEM/EDX

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The silica polymer nano-composites showed large domains of highly ordered stripe-like hexagonally arranged images. The images shown exhibits well-ordered hexagonal arrays of mesopores. HR-TEM images (Fig. 5) of SBA/PS/PPA clearly <sup>40</sup> indicate (shown by arrows) the presence of the polymer coating on the mesoporous material, in addition to this spots seen in the image showed adsorbed PPA. The comparative TEM images of SBA-15 and SBA/PS/PPA clearly depicts the polymer incorporation in mesopores (given in supplementary <sup>45</sup> information). The amount of carbon and phosphorus was also verified by HRTEM/EDX (which was found to be consistent with the theoretical one. Moreover the diffraction pattern (image given in supplementary information) clearly indicates the presence of amorphous nature.



Fig.3 <sup>31</sup>P spectra of mesoporous silica polymer nanocomposite (SBA/PS) and polyphosphoric acid functionalized polymeric silica (SBA/PS/PPA)

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Fig .4 SEM image of polyphosphoric acid functionalized silica polymer nanocomposite(SBA/PS/PPA) with EDX.



Fig.5 TEM image of polyphosphoric acid functionalized silica polymer nanocomposite(SBA/PS/PPA) and EDX

#### 10 FT-IR and Acidity studies

Fig 6 shows vibrational frequencies of neat PPA, SBA/PS, SBA/PS/PPA. A broad peak from 3612 to 3120 cm<sup>-1</sup> for neat PPA can be assigned to PO-H stretching since PPA is an <sup>15</sup> oligomer of  $(OH)_n$ -P- $(O)_n$ -P $(OH)_n$  units. The infrared spectrum of SBA/PS/PPA looks similar to neat PPA and polymer supported SBA spectra<sup>24</sup>. The intensity of O-H stretching from 3300 to3450 cm<sup>-1</sup>in case of SBA/PS/PPA is more than SBA/PS which clearly indicates the incorporation of PPA on the polymeric surface.

<sup>20</sup> Moreover the vibrational frequencies for C=C at 1690 cm<sup>-1</sup> and for C-Cl at 798 cm<sup>-1</sup> for SBA/PS/PPA are consistent with functionalized SBA/PS.

Acidity of SBA/PS/PPA was determined by titration method, wherein 500mg of the SBA/PS/PPA with varied <sup>25</sup> concentrations of PPA as 30%, 20% and 10% was stirred with 0.01M sodium carbonate solution for 12 h and finally the left over basic solution was filtered, washed and titrated with 0.01 M oxalic acid. The titrant value gives the volume of the unused sodium carbonate which was not adsorbed and through this

<sup>30</sup> volume the strength of the SBA/PS/PPA acidic sites was calculated. The number of acidic sites for SBA/30PS/30PPA, SBA/30PS/20PPA and SBA/30PS/10PPA was found to be 38.5mmol/g, 27.36 mmol/g and 13.51 mmol/g respectively also

shown in Table 2.



Fig.6 FT-IR spectra of polyphosphoric acid and functionalized mesoporous silica;(a) PPA, (b) SBA/PS and (c) SBA/PS/PPA

#### **Catalytic Studies**

#### Effect of different variants for optimization

Synthesis of β-amino carbonyl compound over SBA/PS/PPA for obtaining Mannich base was optimized on the model reaction (Scheme 1, R=H).Various reaction parameters were studied to 5 obtain the suitable conditions for the synthesis of β-amino carbonyl compounds (Table 2). The results indicate 94% conversion with 98% selectivity of Mannich base over SBA/PS/PPA compared to 60% conversion and 82% selectivity over SBA/PS/PPA compared to 60% conversion and 82% selectivity over SBA/PPA; the catalytic activity of SBA/PS/PPA increased 10 with increase in PPA content. Also variations in the polymer concentration indicate that 30 wt% polymer loading with equivalent amount of impregnated PPA (about 30 wt %) gave 94% of Mannich base with 98% selectivity.

This may be due to high surface area and better dispersion of active sites over SBA/PS/PPA than SBA/PPA catalyst. Although there was no pronounced difference in the catalytic behavior with increase in the polymer content but maximum activity was achieved with 30 wt% polymer. It is important to mention here that 60% conversion and 65% selectivity was obtained on 20 homogeneous PPA, indicating the necessity of heterogeneous

support for better dispersion of PPA.

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The best catalyst SBA/30PS/30PPA was selected for further studies. An increasing trend of conversion of Mannich base with respect to the weight of both the catalyst SBA/PS/PPA and <sup>25</sup> SBA/PPA was observed. Fig.7 shows an increase in product conversion with increase in catalyst weight uptill 90mg and then became almost constant with further increase in the catalytic sites, depicting the optimum amount of catalytic centers required for bringing about the reaction. However no conversion with <sup>30</sup> 10mg of the catalyst suggests that minimum concentration of the

active site is required for bringing out the conversion.



#### Fig.7 Effect of catalyst weight on the conversion of β-amino <sup>35</sup> carbonyl compound, conditions as given in Table 2

In order to optimize the solvent, different solvents were tried such as water, ethanol, methanol, acetonitrile, chloroform, dichloromethane, toluene, ethylacetate but the best results were 40 achieved, without solvent.

The initial kinetics in the synthesis of  $\beta$ -amino carbonyl compound is a second order nucleophilic reaction (SN<sub>2</sub>) wherein the imine ion formation (Scheme2) is a rate determining step and the stabilization of this intermediate in different solvents leads to

<sup>45</sup> this distinct behavior. Percentage conversion in a polar protic solvent (such as ethanol, methanol) was low, probably due to the solvation of nucleophile (aniline) in these medium and as a result the overall reaction rate gets retarded.

Catalyst	β-amino carb	Acidity (mmol/g)		
	<sup>a</sup> Conversion(%)	<sup>b</sup> Selectivity(%)	(ioi, g)	
PPA	60	65	-	-
SBA/30PPA	60	82	-	-
SBA/20PPA	54	80	-	-
SBA/10PPA	50	80	-	-
SBA/30PS/30PPA	94 (90)	98	241	38.5
SBA/30PS/20PPA	90 (85)	96	310	27.36
SBA/30PS/10PPA	84(77)	94	514	13.51

able 2 Effect of varied catalyst on the conversion of β-amino carbonyl compound (Mannich base)

<sup>*a*</sup> Benzaldehyde (1mmol), Aniline (1mmol), acetophenone (1mmol), no solvent, catalyst (90mg), Temp- 52°C, conversion as detected by GC

<sup>b</sup>selectivity of the product only, () parenthesis in the column (%) conversion indicates % yield, TON= no of moles of product/no of moles of active sites x %yield

<sup>c</sup> TON is the number of moles of desired product formed per number of active centres in a catalyst.

More importantly there was no conversion in water, since the <sup>50</sup> reactants were immiscible. However the polar aprotic solvent

acetonitrile gave high conversion around 75% which may be due to the stabilization of charged intermediate (imine, shown in Published on 14 January 2015. Downloaded by University of California - San Diego on 15/01/2015 04:31:14.

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scheme 2) with lone pairs of acetonitrile but the overall conversion was highest when there was no solvent, this may be due to the low dissolving property of the product Mannich base in

this medium. Moreover the dielectric constant of all the three s reactants aniline=7.3, benzaldehyde= 17, acetophenone=17.4 is high enough for stabilization of iminium ion (Schiff base). In addition, the water formed during the reaction is repelled due

to the presence of hydrophobic catalyst SBA/PS/PPA, and this ultimately does not allow any hindrance in product formation <sup>10</sup> (thereby facilitates the stability of desired product) and consequently stabilizes the product (B). Fig.8 showed the kinetic effect of temperature on % conversion and selectivity of  $\beta$ -amino carbonyl compound. The results concluded that maximum conversion (94%) of the product is achieved at 52°C in 8h, yet <sup>15</sup> the reaction was under observation for 24 h and it was found that no side products were obtained i.e. high selectivity was achieved during the course of the reaction. However further increase in temperature at 80°C leads to decrease in conversion and selectivity of the product which may be due to the formation of <sup>20</sup> the side products (other Mannich bases ) via replacement of

proton on N (given in scheme 2). Thus the favorable temperature was chosen for the reaction.



Fig 8. Effect of time and reaction temperature on the conversion of

β-amino carbonyl compound, conditions as given in Table 2



Scheme 2 Plausible Reaction Mechanism for synthesis of β-amino carbonyl compound (Mannich base).

#### Structure Activity relationship

<sup>5</sup> Careful analysis of the results indicate that polymer coating has a profound role in activity and selectivity of the product formation. The polymer creates the hydrophobic surface and ultimately enhances the diffusion of the products which leads to higher conversion and good selectivity of the β-amino carbonyl
<sup>10</sup> compound. The significant participation of the hydrophobic surface of SBA/PS/PPA during the course of the reaction can be explained via the mechanism of the reaction. During the initial course of synthesis (Scheme 2); a schiff base (an imine, A) via SN<sub>2</sub> mechanism is formed via a nucleophilic reaction between a
<sup>15</sup> protonated benzaldehyde (carbocation) and aniline that further reacts with acetophenone to form Mannich base (B) (shown in Scheme2).

It is important to mention here that the reaction at the initial stages provides maximum schiff base (~70%) with in 2h (Fig.9) <sup>20</sup> which gets subsequently consumed during the course of reaction with acetophenone to form product (B). The percentage of product (B) subsequently grows with time while the % of schiff base (A) drops down to almost zero, however the selectivity of the reaction remains same.



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Fig.9 Comparative study of rate of formation of Schiff base to Mannich base for explaining the route of probable product formation, conditions as in Table 2

<sup>30</sup> However we noticed that the maximum concentration obtained for schiff base (A) is only ~70%, this can be explained due to the three equilibriums participating in the reaction (as shown in scheme 2), although the results for initial kinetics indicate that  $k_1$ is >  $k_1'$ , this is because, the water is constantly removed by the <sup>35</sup> catalyst SBA/PS/PPA (water repelling property due to hydrophobicity) and therefore the reaction moves majorly in forward direction and follows path 1 ( $k_2$ >  $k_1$ ) however we cannot exclude completely the probability of reaction in backward direction ( $k_1'$ ) which is also supported by the observation made <sup>40</sup> towards the end of the reaction wherein some amount of unreacted reactants were found, this might be the reason for the formation of schiff base (A) in low concentration and 94% conversion for Mannich base (B). In addition to this, SBA/PS/PPA catalyst plays a strong role in enveloping the <sup>45</sup> nitrogen site which ultimately retards the side reaction via path 2. Moreover the water removed during the formation of an intermediate reacts with SBA/PS/PPA to form hydronium ion which also contributes in the catalytic activity of the reaction and enhances the % conversion of the product (B). Overall the <sup>50</sup> behavioral properties of SBA/PS/PPA catalyst such as dehydration, enhanced acidity and regeneration of catalyst during the course of reaction play an important role in procuring the higher conversion and selectivity of the product.

#### 55 Reusability and the stability of the catalyst

In order to see the reusability of the catalysts, the catalyst after the reaction was over was filtered thoroughly first with methanol, water and then with acetone. The catalyst was dried at 120°C and subjected for fresh reaction. Recycling of the catalyst was 60 repeated for 5 cycles without significant loss in the activity and selectivity indicating the non-leaching behavior of the acidic contents from the catalyst during the course of the reaction. The optimized conditions were employed for the synthesis of substituted  $\beta$ -amino carbonyl (Table 3) and it was observed that  $_{65}$  the yield of  $\beta$ -amino carbonyl increased when electron withdrawing groups were attached to the carbonyl groups. Furthermore the thermogravimetric analyses Fig10 of the polymer supported PPA (SBA/PS/PPA) demonstrated a good thermal stability up till 600°C than only mesoporous silica 70 (SBA-15) at 365°C and polymer supported silica (SBA/PS) at 410°C.



Fig10. Thermogravimetric analysis of mesoporous silica and 75 functionalized SBA-15, SBA/PS, SBA/PS/PPA materials.

#### Conclusions

Polyphosphoric acid functionalized mesoporous silica polymer nanocomposites were synthesized successfully via wet impregnation method. The precise control of the polymeric Published on 14 January 2015. Downloaded by University of California - San Diego on 15/01/2015 04:31:14.

moiety along with the successful dispersion of polyphosphoric

Table 3 Effect of substituent on the yield of  $\beta$ -amino carbonyl s compound

Aldehyde (R)	Aniline (X)	%yield	
p-NO <sub>2</sub>	Н	97	
p-OMe	Н	72	
p-Cl	Н	82	
p-OH	Н	63	
p-Br	Н	84	
p-CH <sub>3</sub>	Н	68	
Н	p-Br	76	
Н	p-CH <sub>3</sub>	73	

<sup>*a*</sup> The reaction conditions are similar to Table 2 except there is change in the reactants

acid showed mild acidic behavior. The SBA/PS/PPA gave 98% <sup>10</sup> selectivity with 94% conversion of the Mannich base, which is quite an achievement in respect to only 65% selectivity of the  $\beta$ -amino carbonyl product with neat PPA. This can be attributed to the combination of hydrophobicity, textural properties and the presence of bronsted acidic sites on SBA/PS/PPA. Moreover the

<sup>15</sup> probable mechanism explains the role of hydrophobicity in constantly removing the water and in turn increasing the rate of the reaction which leads to good selectivity and activity. Overall PPA functionalized polymer impregnated silica has a potential to show promising results with reactions involving water as one of <sup>20</sup> the product.

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