RSC Advances



View Article Online

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PAPER



Cite this: RSC Adv., 2016, 6, 23981

Synthesis of α -aminophosphonates using a mesoporous silica catalyst produced from sugarcane bagasse ash[†]

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A new green synthesis route is proposed for obtaining a mesoporous material using sugarcane bagasse ash (SCBA) as the silica source. The material obtained was denoted by SBA-16 and its mesostructure was characterized by low-angle X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption techniques. Sulfonic acid groups were introduced to the as-synthesized material, resulting in an acid catalyst denoted by SBA-16/SO₃H. The catalytic activities of SBA-16 and SBA-16/SO₃H were investigated in Kabachnik–Fields reactions, where α -aminophosphonate compounds were produced. The results show that both products can be considered as promising catalysts, where SBA-16/SO₃H showed a slightly better performance than SBA-16.

Received 4th November 2015 Accepted 2nd February 2016

DOI: 10.1039/c5ra23233c

www.rsc.org/advances

1 Introduction

Brazil has the largest area of sugarcane plantations in the world and is a leading exporter of their main products – sugar and ethanol. According to the available data, in 2014 Brazil processed over 630 million tons of raw material, producing about 35.5 million tons of sugar and 28.3 billion liters of ethanol.¹

Sugarcane bagasse ash (SCBA) is generated as a by-product from power plants burning biomass. For each ton of sugarcane bagasse burnt, about 6.2 kg of SCBA is generated,² which is composed mainly of silica.^{3a} Some researchers have reported the use of this by-product in Portland cement,^{3a,b} ceramic materials⁴ and the synthesis of zeolites.⁵ Another use for this cheap silica source is reported in this work, it is the synthesis of SBA-16 type mesoporous silica.

Considering the porous materials, SBA-16 type mesoporous silica (a member of the Santa Barbara Amorphous family) has been reported with a cubic arrangement corresponding to the

Im3m space group.⁶ The synthesis of this material is usually performed under acidic conditions using a non-ionic surfactant, Pluronic F127, as a structure-directing agent and tetraethylorthosilicate (TEOS) as the silica source.6-9 The cage structure of SBA-16 has potential advantages for many applications in different fields, including catalysis,^{7a-c} adsorption,^{7d,e} electronic devices,^{7f,g} and drug delivery,^{7h} and the successful modification of mesoporous silica surfaces with organic functionalities has been reported.^{10a-e} In this context, sulfonic acid groups have been reported as an efficient acid catalyst in organic reactions, e.g. the synthesis of α -aminophosphonate.^{10e} The α -aminophosphonates belong to a class of compounds that have biological activities, which has drawn attention from researchers because of the vast variety of applications, such as pesticides, enzyme inhibitors, antiviral agents, antibiotics, drugs for the treatment of cancer and HIV proteases. Their synthesis has received considerable interest due to their structure being similar to that of amino acids.11

The functionalization of environmentally friendly SBA-16 with sulfonic acid groups and the synthesis of α -aminophosphonates were investigated in this work.

2 Experimental section

2.1 Synthesis of SBA-16

Firstly, the sugarcane bagasse ash (SCBA) was collected from the sugar-alcohol plant located in the region of Maringá City, Paraná, Brazil. The alkali process was carried out to improve the extraction of silicon from the quartz structure. The SCBA was placed in a horizontal furnace and heated at a rate of 20 °C

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra23233c

 min^{-1} from room temperature up to 600 °C, and it was then held at this temperature for 4 h (SCBA600). Furthermore, the compositions (weight percents) in SCBA found by X-ray fluorescence (XRF) were 86.2% SiO₂, 2.8% Al₂O₃, 1.6% P₂O₅, 2.4% K2O, 1.9% TiO2, 1.5% CaO, 2.9% Fe2O3 and 0.7% of trace elements, and in SCBA600 the compositions previously reported were 92.0% SiO₂, 1.6% Al₂O₃, 1.1% P₂O₅, 1.0% K₂O, 0.6% TiO₂, 0.8% CaO, 1.5% Fe₂O₃, and 1.4% of trace elements.⁵ The SCBA600 was used as the silica precursor to synthesize SBA-16, where 4.0 g of SCBA600 were mixed with 6.0 g of NaOH (ratio of 1.5 w/w) to obtain a homogeneous mixture. Then, the mixture was heated in a nickel crucible at atmospheric pressure at 550 °C for 40 minutes. The resultant fused mixture was dissolved in 50 mL of deionized water (solution 1). Then, 4.0 g of surfactant Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, EO = ethylene oxide, PO =propylene oxide, Sigma Aldrich) were dissolved in 120 mL of HCl solution, 2 mol L^{-1} , at room temperature. The mixture was stirred at room temperature until a homogeneous gel solution formed (solution 2). Afterwards, solution 2 was added to solution 1, and this was stirred moderately at room temperature for 20 h. The solid product was filtered, washed with deionized water, and air-dried at 80 °C for 4 h. Finally, the as-prepared white powder was calcinated in air at 550 °C for 6 h, with a heating ramp to reach 550 °C of 1 °C min⁻¹, to remove the surfactant. The sample obtained was denoted as SBA-16.

2.2 Synthesis of the functionalized SBA-16 sulfonic groups

The anchor of the organic group on the mesostructured silica surface occurred *via* a post-synthesis procedure.^{10a} Initially, the SBA-16 was functionalized with thiol (RSH) groups. This was carried out under batch reaction conditions using a 150 mL flask fitted with a stirrer, a thermometer and a reflux condenser at 60 °C. In a typical reaction, 1.0 g of SBA-16 was dissolved in 30 mL of toluene, and then 1.0 mL of 3-mercaptopropyl-trimethoxysilane (MPTMS) was added. After stirring for 24 h, the SBA-16 powder functionalized with thiol groups was recovered, as described in section 2.1. Then, the thiol functionalized SBA-16 was oxidized by slowly adding 30 mL of 30 wt% H₂O₂ solution dropwise over 24 h with moderate stirring at room temperature. The solid product was recovered, as described in section 2.1, and was denoted as SBA-16/SO₃H.

2.3 α-Aminophosphonate synthesis

Initially, the reactions were carried out varying the amount of catalyst (0.003, 0.006, 0.008, 0.01 and 0.02 g). In a typical reaction, 2.0 mmol of aniline, 2.2 mmol of benzaldehyde and 2.0 mmol of diphenylphosphite were mixed in a blank reaction and in the presence of SBA-16 and SBA-16/SO₃H in the amounts indicated above.

Next, the aminophosphonates were synthesized in a similar way, where 0.01 g of catalyst was used in the presence of different solvents (toluene, dichloromethane, chloroform, THF, ethanol and methanol). Finally, after establishing the standard Kabachnik–Fields reaction conditions, other α -aminophosphonates were synthesized following the same protocol, but with benzaldehyde and aniline, as described in Fig. 1.



Fig. 1 General scope for SBA-16 and SBA-16/SO₃H catalyzing the Kabachnik–Fields reaction.

2.4 Characterization techniques

Low-angle X-ray diffraction (XRD) patterns were obtained using Bruker D8-Advance equipment operated at 40 kV and 35 mA with Cu-K α radiation, a wavelength of 1.5406 Å, a 0.01° step size and 2 s per step over the range $0.5^{\circ} < 2\theta < 5^{\circ}$.

Nitrogen adsorption-desorption isotherms were measured at -196 °C on Quantachrome NOVA-1200E Surface and PoroAnalizer equipment. The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) method and the pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) method. Fourier transform infrared (FTIR) spectra were recorded with Thermo Fisher Scientific Nicolet IZ10 equipment in the range of 400–4000 cm⁻¹ using the KBr disc method. Scanning Electron Microscopy (SEM) images were obtained with Shimadzu SSX-550 Superscan equipment and Transmission Electron Microscopy (TEM) images were recorded using JEOL JEM-1400 equipment operated at 120 kV.

The acid capacities of SBA-16 and SBA-16/SO₃H were indicated by temperature-programmed ammonium desorption (NH₃-TPD) and were carried out with AutoChem II 2920 equipment. The α -aminophosphonate products were



Fig. 2 Powder XRD patterns (a), FTIR spectra of the calcined SBA-16 and SBA-16/SO₃H (b), and nitrogen adsorption/desorption isotherms and pore size distribution of the SBA-16 sample (c).

Table 1 Textural and structural properties of SBA-16^a

Sample	$d_{110} ({\rm nm})$	$a_0 (nm)$	$S_{\rm BET} \left({{{\rm{m}}^2}\;{{\rm{g}}^{ - 1}}} ight)$	W(nm)	$V_{\rm t} \left({\rm cm}^3 {\rm g}^{-1} \right)$	$V_{\rm m} \left({\rm cm}^3 {\rm g}^{-1} \right)$	$V_{\rm m}/V_{\rm t}$ (%)	$D_{\rm p} ({\rm nm})$	Ref.
SBA-16	8.48	11.99	576	6.78	0.34	0.10	29	3.27	This work
SBA-16 STD	9.99	14.13	443	9.14	0.24	0.16	67	3.1	8

^{*a*} d_{110} : the plane spacing at Miller indices; a_0 : the cubic lattice parameter $(a_0 = \sqrt{2}d_{110})$; S_{BET} : BET surface area; *W*: wall thickness $(W = \sqrt{3}a_0/2 - D_p)$; V_t : total pore volume; V_m : micropore volume calculated using the BJH method; D_p : pore diameter.



Fig. 3 SEM images (top) and TEM images (bottom) of SBA-16 showing the characteristic plane for a cubic porous structure: (left) [111] and (right) [100] directions.



Fig. 4 NH₃-TPD curves for SBA-16 and SBA-16/SO₃H.

characterized using ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy, using $CDCl_3$ as the solvent and a 300 MHz Bruker AVANCE III HD spectrometer. Chemical shifts are expressed in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz).

Table 2 Performance with different catalyst amounts in the $\alpha\text{-aminophosphonate reactions}^{\alpha}$

	. .		$\mathrm{Yield}^{b}\left(\%\right)$			
Entry	Catalyst (g)	Time (min)	SBA-16	SBA-16/SO ₃ H		
1	0.003	20	74	89		
2	0.006	20	85	95		
3	0.008	20	87	95		
4	0.01	20	90	100		
5	0.02	20	91	100		

 a Reaction conditions: aniline (2.0 mmol), benzaldehyde (2.2 mmol), and diphenyl phosphite (2.0 mmol) in 10 mL of solvent at room temperature. b Isolated yields.

Table 3 Performance with different solvents in the α -aminophosphonate reactions^{α}

Entry	Solvents	$\operatorname{Yield}^{b}(\%)$	
1	Toluene	95	
2	Dichloromethane	100	
3	Chloroform	98	
4	THF	87	
5	Ethanol	70	
6	Methanol	79	

^{*a*} Reaction conditions: aniline (2.0 mmol), benzaldehyde (2.2 mmol), diphenylphosphite (2.0 mmol), SBA-16 (0.01 g), solvent (10 mL), room temperature, 20 minutes. ^{*b*} Isolated yields.

3 Results and discussion

3.1 Structure characterization and morphology

Fig. 2(a) shows the powder X-ray diffraction patterns of SBA-16 and SBA-16/SO₃H, prepared as described previously.

Both show a single intense diffraction peak at 2θ values of 1.01 and 1.04°, respectively, which belongs to the cubic phase of the (1 1 0) plan. The slight shift to a higher 2θ value is due to the grafting of sulfonic acid groups into the SBA-16 pores.¹² From Bragg's law ($n\lambda = 2d \sin \theta$) and the relationships $(1/d_{hkl}^2 = (h^2 + k^2 + l^2)/a_0^2)$ and ($a_0 = \sqrt{2}d_{110}$) between the cubic lattice parameter (a_0) and the plane distance (d_{hkl}) at different Miller indices (hkl), if the first peak belongs to the (110) diffraction peak of the cubic phase, the diffraction peaks should appear at $2\theta_{200} = 1.433^\circ$ and $2\theta_{211} = 1.755^\circ$ for SBA-16 and $2\theta_{200} = 1.47^\circ$ and $2\theta_{211} = 1.80^\circ$ for SBA-16/SO₃H. Our second diffraction peaks in the experimental data match the theoretical results very well with $2\theta = 1.425^\circ$ and 1.471° , respectively, and a third



Entry	Aldehyde	Amine	Product	SBA-16 (yield ^{<i>a</i>} /time ^{<i>b</i>})	SBA-16/SO ₃ H (yield ^{<i>a</i>} /time ^{<i>b</i>})
1	СНО	NH ₂	O OPh NH P OPh	100/20	100/20
2	CHO CI	NH ₂	O, OPh NH, P, OPh CI	90/30	93/30
3	CHO Br	NH ₂	O OPh NH P OPh Br	92/30	98/30
4	CHO F	NH ₂	O OPh NH P OPh F	75/45	78/45
5	СНО	NH ₂	CI NH P OPh	87/30	90/30
6	СНО	NH ₂ Br	Br NH P OPh	93/45	95/30

^{*a*} Isolate yields (%). ^{*b*} Time reaction (min).



Fig. 5 Plausible mechanism for the synthesis of α -amino-phosphonates over a SBA-16 or SBA-16/SO₃H catalyst.

small peak for SBA-16/SO₃H at 1.79° only. Therefore, the XRD patterns of SBA-16 can be indexed as $(1\ 1\ 0)$, $(2\ 0\ 0)$, and $(2\ 1\ 1)$ reflections, corresponding to a cubic *Im3m* structure.^{7h}

Fig. 2(b) shows the Fourier transform infrared (FTIR) spectra of SBA-16 and SBA-16/SO₃H. They show the typical absorption peaks related to groups of a mesoporous silica network around 3700–3100, 1300–1000, 1640, 960, 810, and 460 cm⁻¹. The bands around 460 cm⁻¹ and 810 cm⁻¹ are assigned to the symmetric stretching and rocking modes of the Si–O–Si vibrations. The broad band at 1300–1000 cm⁻¹ (with the peak around 1080 cm⁻¹) is assigned to the asymmetric stretching mode of the Si–O–Si moiety.^{13*a*,*b*} The shoulder at 960 cm⁻¹ is assigned to silanol groups existing in the structure of the material. The broad band at 3100–3700 cm⁻¹ is associated with the –OH stretching vibration mode of the silanol groups and the water hydroxyl groups and the other band observed at 1640 cm⁻¹ is assigned to the vibrations of adsorbed water molecules.^{13*c*} The characteristic IR signals of the sulfonic acid group in the SBA-16/SO₃H sample overlap at 920 cm⁻¹ (*v*S-O), 1425 cm⁻¹ (*v*_{as}S= O), and 3000–3222 cm⁻¹ (*v*_(O-H)) and the clear peak at 2340–2360 cm⁻¹ is described as the first overtone of the O–H bending vibration mode of the SO₃H groups engaged in a strong hydrogen bond.^{13d}

The adsorption/desorption isotherms for SBA-16 are shown in Fig. 2(c). The sample exhibits isotherms of type IV with a hysteresis adsorption/desorption of type H2, according to the IUPAC classification, characteristic of mesoporous materials.¹⁴ The textural and structural properties are shown in Table 1. The pore wall thickness of SBA-16 is calculated by $W = \sqrt{3}a_0/2 - D_p$,⁹ where a_0 and D_p are the cubic lattice parameter and the pore diameter, respectively.

The specific surface area of 576.11 m² g⁻¹ is close to the values obtained by the conventional synthesis of SBA-16, *i.e.* using a conventional silica source $(338-526 \text{ m}^2 \text{ g}^{-1})$.^{8,9} Moreover, the value of the pore diameter (3.27 nm) and the percentage of micropore volume (29%) reaffirm the meso-structure of SBA-16.

SEM and TEM were employed for the investigation of the morphological structure of SBA-16 (Fig. 3). The SEM images show the irregular morphology for SBA-16, synthesized without hydrothermal treatment. The TEM images show the porous structure along the [111] direction (bottom left image) and along the [100] direction (bottom right image). A well-ordered cubic porous structure 3–5 nm in diameter can be observed, corresponding to a cubic *Im*3*m* structure.⁸ This value is in good agreement with the analysis from XRD (Fig. 2(a)) and N₂ physisorption (Fig. 2(c)).

A further increase in the catalyst loading up to 0.02 g did not result in any significant change in the yield.

Table 3 shows the influence of solvents in the synthesis of the α -aminophosphonates. Toluene, dichloromethane and chloroform presented the highest yields (Table 3, entries 1–3). Therefore, we established DCM as the standard solvent for further Kabachnik–Fields reactions with starting materials of diphenylphosphite (2.0 mmol), aniline 4-derivatives (2.0 mmol) and benzaldehyde 4-derivatives (2.2 mmol), and 0.01 g of the catalyst.

Fig. 4 shows the NH₃-TPD curves for SBA-16 and SBA-16/SO₃H. A large desorption peak centered around 190 °C was observed for SBA-16/SO₃H. Note that no desorption peak appeared in the NH₃-TPD curve of the unmodified SBA-16, which confirms that the peak for SBA-16/SO₃H can be assigned to NH₃ desorption from the sulfonic acid groups. In addition, another peak between 250 and 500 °C occurs, but this indicates the decomposition of sulfonic acid groups in temperatures above 200 °C.¹⁵

3.2 Catalyst tests

A blank reaction was carried out without any catalyst for 60 minutes and the compound of interest was not obtained. Table 2 shows the performance of the α -aminophosphonate synthesis with various catalyst loadings. The amount of SBA-16 and SBA-16/SO₃H varied from 0.003 to 0.02 g. The yields increased

gradually until the catalyst's best performance with 0.01 g. The data for the other reactions are presented in Table 4 with a comparison between SBA-16 and SBA-16/SO₃H as the heterogeneous catalyst (Tables 3 and 4). We could observe that the catalyst produced the α -aminophosphonates in good and excellent yields. Therefore, regarding the structural differences of the SBAs, the presence of the sulfonic group did not result in any considerable improvement in the yields for the Kabachnik-Fields reaction. Through the analysis of these data, we concluded that the catalysis was preferentially performed in the Brønsted acid sites. The presence of the silanol group in SBA-16 causes a positive charge density, attributed to the hydroxyl group, that can be considered as a very weak Brønsted acid site.¹⁶

On the other hand, the SBA-16/SO₃H catalyst gives a better performance compared to SBA-16, which is expected because of its strong acid sites attributed to the sulfonic acid groups, in accordance with the TPD-NH₃ analysis. Besides, to the best of our knowledge, the imine synthesis (intermediate II) is the slow step for Kabachnik–Fields reactions.

Therefore, we may infer that the presence of the catalyst resulted in an improvement in the reaction rate for the synthesis of this intermediate. With this information, we devised a plausible mechanism for these reactions. Firstly, the benzaldehyde will interact with SBA, specifically in the Brønsted acid sites (intermediate I). Secondly, the aniline will attack intermediate I and, after the removal of water, the imine intermediate is obtained (intermediate II). After this step, intermediate II will undergo an attack from the phosphite, which will produce the α -aminophosphonate. This plausible mechanism is in accordance with the literature and it is shown in Fig. 5.^{17a,b}

The products and results of the synthesis of the α -aminophosphonates using heterogeneous catalysts SBA-16 and SBA-16/SO₃H are given in Table 4.

4 Conclusions

In the present work, we have proposed a new approach for the synthesis of SBA-16 type mesoporous silica from sugarcane bagasse ash. The as-synthesized material has good textural and structural properties, and this is a good alternative use for SCBA. Furthermore, the material obtained was successfully functionalized with sulfonic acid groups, allowing an improvement in its catalytic activity for the synthesis of α -aminophosphonates.

Acknowledgements

We gratefully acknowledge the Brazilian agencies (CAPES/ CNPQ) for financial support.

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