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Alkyl surface modification of nanoporous silica SBA-15 by click chemistry to obtain triazole products

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ABSTRACT: In this study, Santa Barbara Amorphous (SBA-15) mesoporous silica has been functionalized with aminopropyl groups that were converted to propargyl-bearing moieties through the reaction with propargyl bromide. The material then underwent an efficient Cu(I)-catalyzed azide alkyne click reaction with sodium azide in order to obtain the corresponding triazole products. The covalent modification of mesoporous silica surface with organic functional groups was confirmed by different characterization techniques including Fourier transform infrared spectroscopy, thermogravimetric analysis, Scanning electron microscopy, Transmission electron microscopy, N_2 adsorption-desorption isotherms and Raman spectroscopy. The results have confirmed that SBA-15 was successfully functionalized with organic moieties. No change in the periodic structure of the SBA-15 silica support was observed throughout the grafting procedure. Surface area, pore size and pore volume decreased by attaching functional groups to the pore surface. This approach provides a simple and convenient route to efficiently functionalize a wide range of new structures on the surface of SBA-15.

Keywords: *Click reaction; Functionalized SBA-15; Huisgen 1,3-dipolar cycloaddition; Mesoporous silica; Propargyl bromide*

INTRODUCTION

Recently, mesoporous silica materials have attracted the attention of researchers worldwide. Their environmental compatibility, reusability, high selectivity, and excellent (chemical and thermal) stability are remarkable properties that made them promising candidates for widespread applications in important areas such as catalysis (Mohammadi Ziarani, *et al.*, 2015b), sensor design (Lashgari, *et al.*, 2017) and medicine (Fathi Vavsari, *et al.*, 2015). Santa Barbara Amorphous (SBA-15) introduced by Stucky and co-workers (Zhao, *et al.*, 1998), is a kind of mesoporous silica featured by a highly-ordered porous and size-controlled structure, high specific surface area, great pore wall thickness, and wide accessibility that makes it a favorable inorganic support (Gholamzadeh, *et al.*, 2017, Garg, *et al.*, 2016, Xie, *et al.*, 2015). SBA-15 stands as a highly functional platform that can fulfill multiple purposes: the solid support renders the rigidity, high specific surface area, and mechanical stability whereas the organic component introduces desired chemical properties.

Copper-catalyzed azide-alkyne 1,3-dipolar cycload-

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dition reaction as one of the best click reactions to date, is an area of organic chemistry that has received remarkable interest in recent years and as a result, a number of publications have been devoted to this topic in last few years (Amblard, *et al.*, 2009, Rahimifard, *et al.*, 2017, He, *et al.*, 2012, Mohammadi Ziarani, *et al.*, 2015c, Mohammadi Ziarani, *et al.*, 2016, Wei, *et al.*, 2016, Aioub, *et al.*, 2017, Kacprzak, *et al.*, 2016). The key advantages of click reaction are its simplicity, compatibility with a broad repertoire of functional groups, and high yields. Recently, some significant researches on clickable mesoporous silica have been reported in the literature. For example, in a study by Pathak and Singh, click reaction was found to be modular approach for the synthesis of highly efficient and recoverable D-2PA-Pd(II)@SBA-15 catalyst (Pathak and Singh, 2017). In another study, Stack and coworkers reported the efficient covalent attachment of ferrocene, pyrene, tris(pyridylmethyl)amine (TPA), and iron porphyrin (FeTPP) to the mesoporous silica through click reaction (Nakazawa, *et al.*, 2012). Badiei's team designed a novel organic-inorganic hybrid material by grafting 8-hydroxyquinoline on the surface of SBA-15 via click reaction for optical sensing of Zn^{2+} and CN^- ions (Karimi, *et al.*, 2016). The most common approach is to introduce the azide functionality into the mesoporous materials (Khaniani, *et al.*, 2012, Malvi, *et al.*, 2009, Nakazawa and Stack, 2008, Schlossbauer, *et al.*, 2008). Previously, we reported the preparation of SBA-15 mesoporous silica functionalized with different organic groups such as sulfonic acid (Mohammadi Ziarani, *et al.*, 2015a) and amine (Mohammadi Ziarani, *et al.*, 2017). This work aims to develop an alternative approach to the synthesis of clickable SBA-15 (Scheme 1). The surface of SBA-15 was modified with 3-aminopropylsilyl groups, in which the amine moieties were converted to terminal alkynes through the reaction with propargyl bromide. Further functionalization of the clickable alkyne labeled SBA-15 was achieved through the reaction with sodium azide to obtain the corresponding triazole products (Scheme 1). It is noteworthy to mention here that, synthesis of alkyne containing SBA-15 materials would be very useful in the development of functional materials. The presence of an organic alkyne on SBA-15 gives a handle to anchor various organic moieties (Huang, *et al.*, 2010).

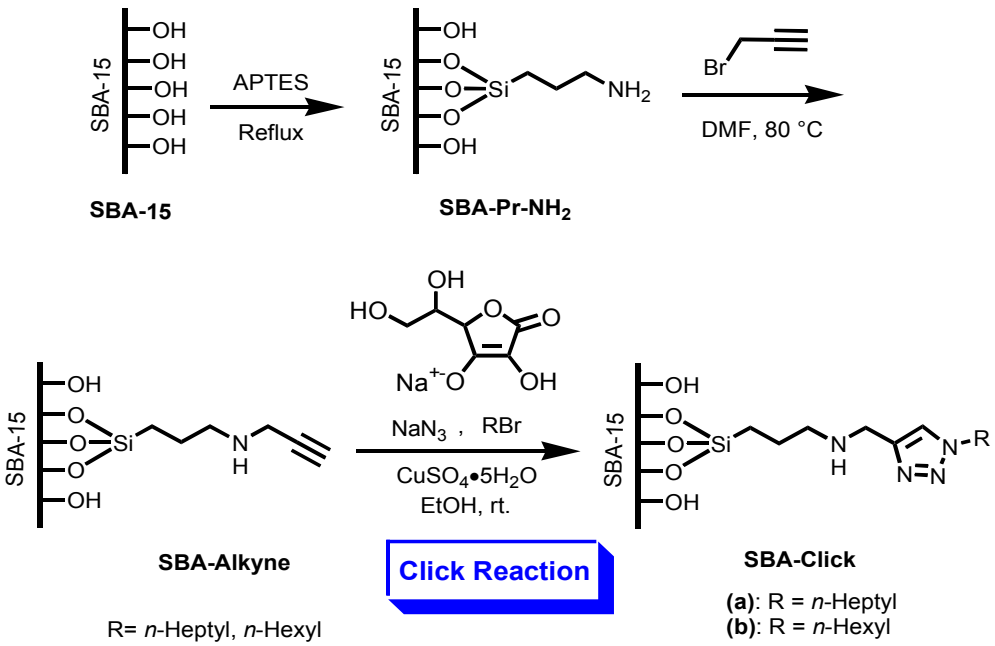
EXPERIMENTAL

MATERIAL AND METHODS

Pluronic P123 triblock copolymer was purchased from Aldrich. Tetraethyl orthosilicate (TEOS), (3-aminopropyl)triethoxysilane (APTES), propargyl bromide, and sodium azide were obtained from Merck Company. All solvents were obtained from Merck Company and were used with no purifications. IR spectra were established from KBr disk using a FT-IR Bruker Tensor 27 instrument. Raman spectra were documented using a Senterra Bruker instrument. N_2 adsorption-desorption isotherms were measured using a BELSORP-mini II instrument at liquid nitrogen temperature (-196°C). Degassing process for all samples was performed at 100°C before the measurements. Thermogravimetric analyses (TGA) were carried out by a TGA Q50 V6.3 Build 189 instrument from ambient temperature to 1000°C with a ramp rate of 10°C min^{-1} in the air. The Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) equations were applied on sorption data using BELSORP analysis software to calculate the physical properties of materials such as the specific surface area, pore diameter, pore volume and pore size distribution. Field Emission Scanning Electron Microscope (FE-SEM) analysis was performed on a Hitachi S-4160 operated at 30 kV. Transmission electron microscopy (TEM) analysis was performed on a Tecnai G^2 F30 at 300 kV. Samples were dispersed in ethanol using an ultrasonic bath and a drop of the ethanol mixture was placed on a lacey carbon-coated copper grid for analysis.

General procedure for the synthesis and functionalization of SBA-15

SBA-15 was prepared according to previously published procedure (Lashgari, *et al.*, 2014). The synthesis procedure for aminopropyl grafting of SBA-15 (SBA-Pr-NH_2) was the same with our previous work (Mohammadi Ziarani, *et al.*, 2012). For the synthesis of SBA-Alkyne, first, 1 g of SBA-Pr-NH_2 was activated at 100°C under vacuum to remove any surface humidity. Then, it was stirred in dry N,N-dimethyl-



Scheme 1. Preparation of clickable SBA-15.

formamide (DMF) (20 mL) at 80°C in which excess amount of propargyl bromide was gradually added in three steps. The reaction was carried out at 80°C for 24 h. Subsequently, the resulting solid product was filtered off and washed sequentially with DMF. Finally, the excess of propargyl bromide was removed using ethanol in soxhlet extractor system to isolate alkyne containing SBA-15 material (denoted as SBA-Alkyne). To a mixture of SBA-Alkyne (0.25 g), NaN_3 (4 mmol), and n-bromoalkane (4 mmol) in 50 mL of EtOH, $CuSO_4$•$5H_2O$ (0.25 g) and sodium ascorbate (0.4 g) as Cu(I) catalyst were added and the reaction mixture was stirred for 24 h at room temperature. Afterward, the mixture was filtered off and washed with ethanol to remove the catalyst. Then the products were dried to prepare the final SBA-Click (a) and SBA-Click (b) (Scheme 1).

RESULTS AND DISCUSSION

Herein, the click functionalization of SBA-15 support through the copper-catalyzed azide-alkyne cycloaddition reaction was studied. The nucleophilic substitution reaction between SBA-Pr-NH_2 and propargyl bromide was first investigated in the presence of two different solvents (DMF and toluene) and different bases including Et_3N and K_2CO_3. As shown in Table 1, the most encouraging result was obtained when DMF was employed as the solvent in the absence of a base catalyst. In the presence of other solvents and bases no product was obtained.

For structural proof of the presence of the alkyne moieties covalently bonded onto the SBA-15 surface, we carried out FT-IR spectroscopy. The spectrum of SBA-Alkyne contains the characteristic peaks of silica

Table 1. Different conditions for nucleophilic substitution on the surface of amino-functionalized SBA-15.

Entry	Solvent (dry)	Base	Time (h)	Product
1	DMF	-	24	SBA-Alkyne
2	Toluene	-	24	No reaction
3	Toluene	Et_3N	24	No reaction
4	Toluene	K_2CO_3	24	No reaction
5	DMF	Et_3N	24	No reaction

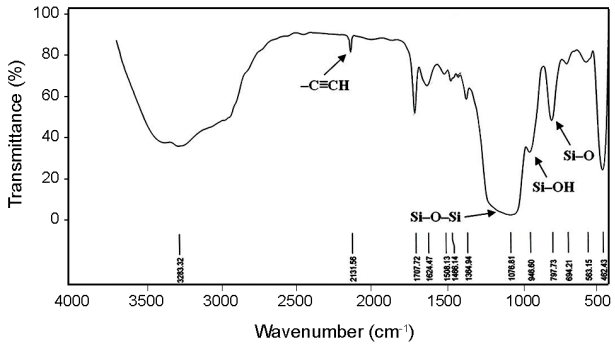


Fig. 1. FT-IR Spectrum of SBA-Alkyne.

framework of SBA-15 located at 797, 946, and 1076 cm^{-1}, corresponding to the typical Si–O–Si bonds. The bands due to the stretching vibrations of methylene (-CH_2-) in propyl chain are present within the range of 2880–2960 cm^{-1}. Physically adsorbed water molecules showed a peak around 1624 cm^{-1}. The alkyne moiety of the SBA-Alkyne material was also characterized by IR spectroscopy. The presence of an intense absorbance at 2131 cm^{-1} is a characteristic of stretching vibration of any alkyne moieties (Fig. 1).

Fig. 2 shows the Raman spectrum of SBA-Alkyne. The band at 2134 cm^{-1} is attributed to –C≡CH vibrations, confirming that the alkyne was attached onto the surface of SBA-15 (Socrates, 2004).

SBA-Click product was prepared from the reaction of SBA-Alkyne, NaN_3, and n-bromoalkane under vigorous stirring for 24 h at room temperature. In this reaction, $CuSO_4$•$5H_2O$/Na ascorbate system was added to the mixture for in situ formation of copper (I) species as the catalysts. Subsequently, excess amount of $CuSO_4$ and sodium ascorbate were separated by simple filtration, and the final click product was isolated as powder and purified by ethanol.

Fig. 3 shows the FT-IR spectrum of click product

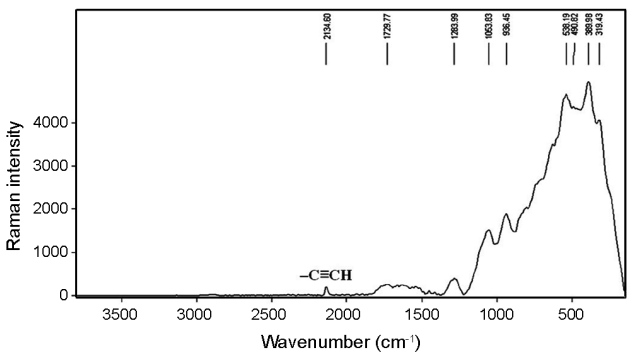


Fig. 2. Raman spectrum of SBA-alkyne.

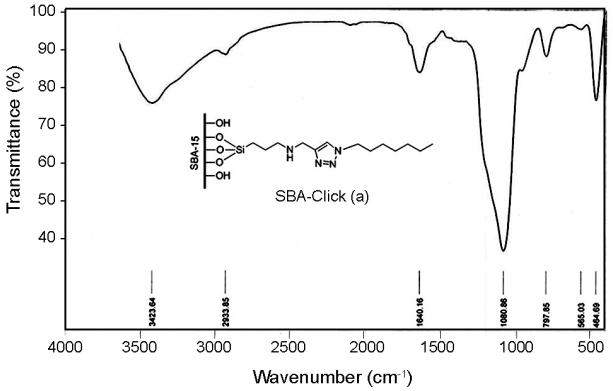


Fig. 3. FT-IR spectrum of SBA-Click (a).

SBA-Click (a). The peaks at 1640 cm^{-1} are assigned to the double bond vibration of C=C in triazole rings but overlapping with physically adsorbed water molecules prevents unambiguous observation of this band. The aliphatic –CH_2 band was observed at about 2933 cm^{-1} and the absence of alkyne peak at 2131 cm^{-1} was evidence of the click reaction. The FT-IR spectrum of click product SBA-Click (b) is provided in Fig. S1.

Further information about the grafting of organic groups onto the surface of SBA-15 could be extracted from thermogravimetric analyses data. The TGA

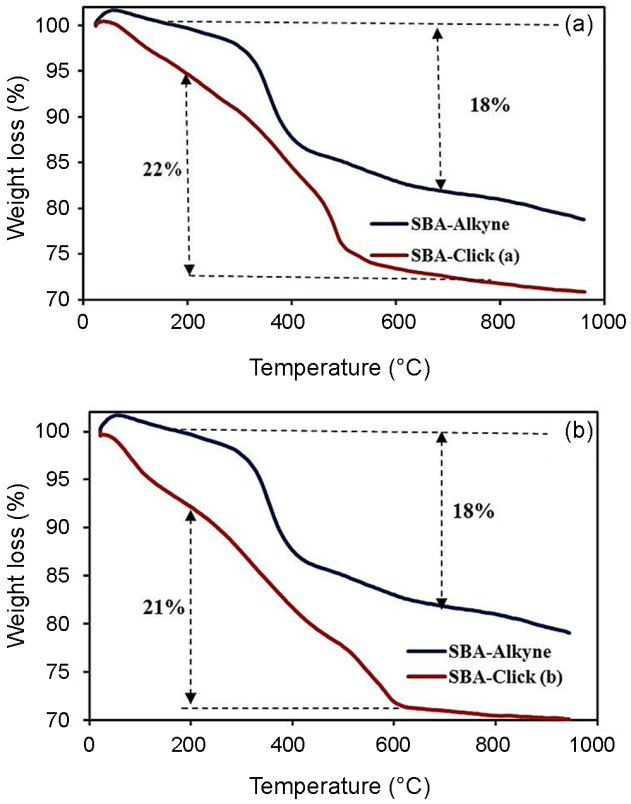


Fig. 4. TGA curves of Top: SBA-Alkyne and SBA-Click (a) and Bottom: SBA-Alkyne and SBA-Click (b).

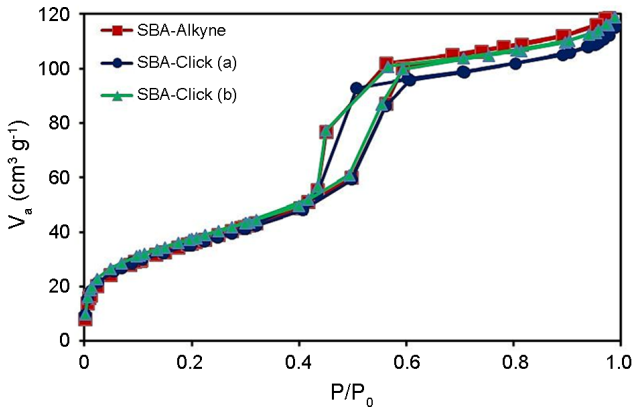


Fig. 5. Nitrogen adsorption-desorption isotherms of SBA-Alkyne, SBA-Click (a) and SBA-Click (b).

profiles of SBA-Alkyne and click products are illustrated in Fig. 4. The initial exceeding of the weight of SBA-Alkyne from 100% is due to the buoyancy effect (Newkirk, 1960). Both TGA curves of click products showed an initial weight loss around 150 °C due to the loss of residual water and other volatiles from the pore channels. The subsequent major weight losses between 200 and 600°C generally correspond to the thermal dissociation of grafted organic functional groups. According to TGA analyses, the amount of the propyl alkyne moieties incorporated into the mesoporous silica in the SBA-Alkyne sample was estimated to be 1.9 mmol g^{-1}. The amount of propyl triazole moieties in SBA-Click (a) and SBA-Click (b) products were estimated to be about 0.95 and 0.97 mmol g^{-1}, respectively.

In order to investigate the pore structure of SBA-15 after functionalization steps, the N_2 adsorption-desorption isotherms of the prepared samples were measured (Fig. 5). The corresponding isotherms exhibit a

Table 2. Characteristics of the synthesized materials derived from nitrogen adsorption-desorption isotherms.

Sample	Textural properties		
	S_{BET} (m^2/g)	V_{total} (cm^3/g)	D_{BJH} (nm)
SBA-15	481	1.3	5.9
SBA-Pr-NH_2	356	1.0	3.6
SBA-Alkyne	134	0.17	2.5
SBA-Click (a)	132	0.16	2.4
SBA-Click (b)	129	0.16	2.4

S_{BET}: specific surface area;

V_{total}: total pore volume;

D_{BJH}: average pore diameter.

characteristic type IV isotherms with H1-type hysteresis loops as defined by IUPAC (Sing, *et al.*, 1985). The isotherms appear similar to their parent SBA-15 material (Fig. S2), which implies that original structure of SBA-15 was preserved after functionalization steps by organic moieties. The pore diameter, BET surface, and the pore volume are given in Table 2 which shows a trend of decreasing in all three parameters due to the attachment of organic moieties within the mesopores of SBA-15.

Fig. 6 illustrates the SEM and TEM images of SBA-Pr-NH_2. SEM image (Fig. 6, left) displays uniform particles about 1 µm. The same morphology was observed for SBA-15. It can be concluded that morphology of solid was saved without change during the surface modifications. On the other hand, the TEM image (Fig. 6, right) reveals ordered arrays of channels resembling the configuration of the pores of SBA-15.

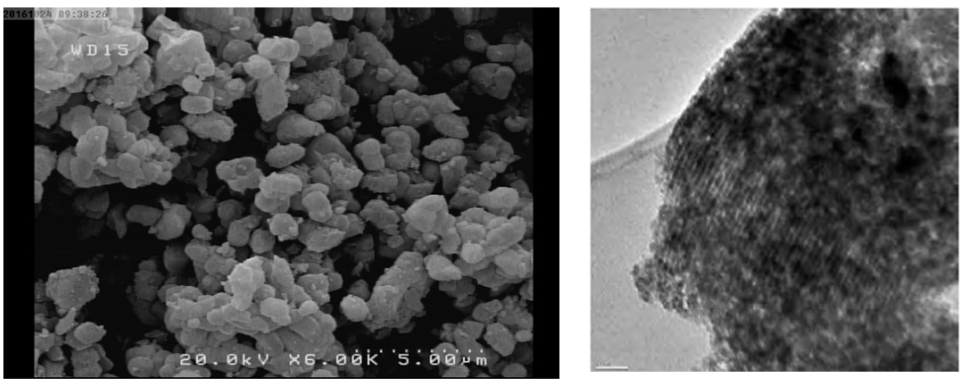


Fig. 6. SEM (left) and TEM (right) images of SBA-Pr-NH_2.

CONCLUSIONS

The azide-alkyne click reaction was found to be a powerful tool for the functionalization of the surface of mesoporous silica. SBA-15 was successfully functionalized with alkyne groups and underwent Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction with sodium azides. The incorporation of the organic functionalities and preservation of SBA-15 structure were confirmed by different characterization techniques including FT-IR, TGA, SEM, TEM, N_2 adsorption-desorption isotherms and Raman spectroscopy. This approach provides a convenient route to efficiently functionalize a wide range of new structures on the surface of SBA-15 mesoporous silica.

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