



# Mesoporous SBA-15 supported silver nanoparticles as environmentally friendly catalysts for three-component reaction of aldehydes, alkynes and amines with glycol as a “green” solvent

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## ARTICLE INFO

### Article history:

Received 25 September 2009

Received in revised form 1 February 2010

Accepted 4 March 2010

Available online 10 March 2010

### Keywords:

A<sup>3</sup>-coupling reaction

Glycol

Heterogeneous catalysis

SBA-15

Silver nanoparticles

## ABSTRACT

The mesoporous SBA-15 supported silver nanoparticles catalyst system with a highly ordered hexagonal mesostructure was prepared by an in situ reduction method using hexamethylenetetramine as mild and efficient reducing agent. These AgSBA-15 materials act as environmentally friendly catalysts in A<sup>3</sup>-coupling reactions of aldehydes, amines, and terminal alkynes with glycol as a “green” solvent. It is also found that the maximum reaction yield has been obtained for an average Ag-nanoparticle size of about 8 nm. The catalyst could also be recovered easily and used repetitively four times without significantly affecting the catalytic activity. The heterogeneous catalysts were fully characterized by N<sub>2</sub> adsorption and desorption, XRD, TEM, ICP and XPS.

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## 1. Introduction

Three-component coupling reactions of aldehyde, alkyne, and amine (A<sup>3</sup>-coupling) have attracted much attention, because their coupling products, propargylamines, are versatile building blocks for the synthesis of N-containing heterocyclic compounds such as pyrrolidines, oxazoles and pyrroles [1–7], and key intermediates for natural product synthesis [8–11]. There has been an ongoing interest to develop homogeneous transition metal salt catalysts for this three component (A<sup>3</sup>-coupling) reaction, such as Cu(I) salts [4,12–20], Ag(I) salts [1,21–23], Au(I)/Au(III) salts [18,24–27], Fe(III) salts [28], and Ir, In and Zn compounds [29–34]. Ag(I) and Cu(I) salts in ionic liquids have also been developed to achieve the recyclability of the catalysts [35,36]. However, using the above-mentioned protocols, reactions were carried out in either toxic solvent like toluene, or expensive system, such as ionic liquids.

Heterogeneous catalysis offers the opportunity for easy separation and recycling of the catalyst. Thus, the development of improved synthetic methods for the preparation of propargylamines remains an active research area. As heterogeneous

catalysis systems, hydroxyapatite-supported copper (Cu-HAP), layered double hydroxide supported gold (LDH-AuCl<sub>4</sub>) and heteropolyacid-supported silver (Ag-HPA) [37–39], zinc dust, AgY zeolite, nanocrystalline CuO and CeO<sub>2</sub>- or ZrO<sub>2</sub>-stabilized Au(III) [26,40–42] were successfully used to catalyze A<sup>3</sup>-coupling reactions with reusability of catalysts. Recently, Ag-, Au- and Cu-nanoparticles as reusable catalysts have also been reported [43–46]. However, almost all of these A<sup>3</sup>-coupling reaction protocols were carried out in toxic solvents. It is desirable to develop highly efficient catalysts for A<sup>3</sup>-coupling reactions in environmentally friendly medium. Most recently, environmentally friendly A<sup>3</sup>-coupling reactions in water [18,47] or under solvent-free conditions [48–51] have been described. However, no mesoporous silica supported Ag-nanoparticles as reusable catalyst for A<sup>3</sup>-coupling reactions in environmentally friendly medium has so far been reported. According to their narrow pore size distribution, high specific surface area (600–1000 m<sup>2</sup> g<sup>-1</sup>) and large pore volume, SBA-15 mesoporous silica materials are promising catalyst supports [52–54]. An in situ reduction method using hexamethylenetetramine (HMTA) as mild and efficient reducing agent for the preparation mesoporous SBA-15 supported silver nanoparticles has been recently disclosed by our group [55].

Herein, we report a novel recyclable SBA-15 supported silver nanoparticles catalyst for A<sup>3</sup>-coupling reaction. Furthermore, we first demonstrate the silver nanoparticles-catalyzed A<sup>3</sup>-coupling reactions can be carried out in a more environmentally benign

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medium. As far as we know, this kind of silver nanoparticles-catalyzed “green” reaction has not been reported before.

## 2. Experimental

All reagents were purchased from commercial sources and were used as received.

### 2.1. Catalyst preparation

Pure mesoporous silica SBA-15 material was hydrothermally synthesized using tri-block copolymer pluronic P123 as a template in acidic conditions. The gel solution was prepared by dispersing 8 g of P123 in 60 g of distilled water, followed by 15 min of vigorous stirring at 40 °C. The resulting solution was mixed with 48 g of HCl (37%) and 190 g of H<sub>2</sub>O and stirred for another 17 h. Finally, 21.2 g of tetraethylorthosilicate (TEOS) solution was added dropwise in the gel mixture at 40 °C with stirring for 9 h before being placed in a Teflon autoclave at 100 °C for 12 h. After the completion of synthesis, the product was filtered, washed with distilled water, and air-dried overnight at 50 °C. The solid was calcined at 550 °C (heating rate 2 °C min<sup>-1</sup>) for 5 h.

Supported AgSBA-15 catalysts were synthesized via in situ reduction method using hexamethylenetetramine (HMTA) as reducing agent. A series of AgSBA-15 catalysts were prepared as follows: 1 g of tri-block copolymer pluronic P123 was dissolved in 30 g of H<sub>2</sub>O to get a clear solution. Thereafter, 3 g of nitric acid was added, and the solution was stirred at 35 °C for 1 h. Then, 0.35 g of HMTA and various amounts of AgNO<sub>3</sub> (such as 0.035, 0.070, 0.10, 0.125, 0.15, 0.175, 0.20, 0.25, 0.50, and 1.0 g) were added, and the resulting mixture was stirred for another 3 h at 35 °C while darkening. After 2.13 g of TEOS was added and continuously stirred at 35 °C for 20 h while darkening, the mixture was crystallized at 100 °C for 48 h under static and darkening conditions. The resulting solid was filtered, washed several times with water and ethanol, and then dried for 10 h at 50 °C under vacuum condition. Finally, the solid was calcined in air at 550 °C (heating rate 2 °C min<sup>-1</sup>) for 5 h. The corresponding AgSBA-15 catalysts were named as AgSBA-15-1, AgSBA-15-2, AgSBA-15-3, AgSBA-15-4, AgSBA-15-5, AgSBA-15-6, AgSBA-15-7, AgSBA-15-8, AgSBA-15-9, and AgSBA-15-10, respectively.

### 2.2. Catalyst characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a Philips X'Pert PRO SUPER diffractometer operating with nickel-filtered Cu-K $\alpha$  radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed on a ESCALAB 250 high performance electron spectrometer using monochromatized Al-K $\alpha$  excitation source ( $h\nu = 1486.6$  eV). Transmission electron micrographs (TEM) were taken on a JEOL-2010 electron microscope operating at 200 kV. N<sub>2</sub> adsorption and desorption isotherms were obtained at -196 °C on an Omnisorp 100CX instrument. The specific surface area was calculated using the BET model. The content of Ag loaded in mesoporous silica was determined by Atomscan Advantage inductively coupled high frequency plasma atomic emission spectrometry (ICP-AES).

### 2.3. Catalytic studies

Typical procedure for the A<sup>3</sup>-coupling reaction: in a 50 ml round bottom flask, aldehydes (1.0 mmol), secondary amines (1.2 mmol) and alkynes (1.5 mmol) in glycol (5 ml) were mixed and stirred under a nitrogen atmosphere. To this, AgSBA-15 catalyst (5 mol%) was added. The resulting solution was refluxed at 75 or 100 °C for

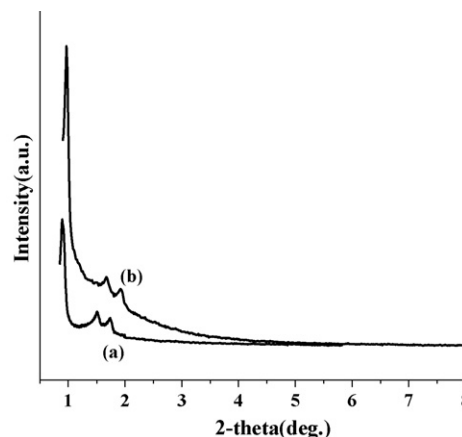


Fig. 1. Small angle X-ray diffraction patterns of pristine SBA-15 (a) and AgSBA-15 (b) samples.

the appropriate time mentioned in Table 4. The progress of reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled and extracted with ether for three times, and the ether layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the ether was removed under reduced pressure to afford the crude product. The crude product was subjected to purification by silica gel column chromatography using ethyl acetate and petroleum ether (1:10) as an eluent to yield the propargylamines. The structures of all the products were unambiguously established on the basis of their <sup>1</sup>H NMR data (all <sup>1</sup>H NMR spectra were recorded on an Avance AV300 spectrometer using CDCl<sub>3</sub> as solvent).

## 3. Results and discussion

### 3.1. Characterization of the catalysts

The calcined AgSBA-15 catalysts retained its hexagonally packed porous structure as shown in the small angle XRD pattern (Fig. 1), one major peak at  $2\theta \approx 1^\circ$  together with two additional peaks can be observed, which are the characteristic of the hexagonal mesoporous structure of SBA-15. Different from the other reports, in which the peak intensities usually decrease after guest loading, comparatively, the intensity in this case has somewhat increase after loading Ag, especially for (1 0 0) reflection. It is more likely that the sample thickness/homogeneity was different in the XRD experiments. Interestingly, after loading Ag, the (1 0 0) peak is shifted to higher  $2\theta$  value, which is attributed to the network shrinkage (the  $a_0$  parameters of SBA-15 and AgSBA-15 are 11.55 and 10.59 nm, respectively). AgNO<sub>3</sub> could be adsorbed on the EO moiety surfaces to form a complex with the micelles formed by P123 in aqueous solution, which possibly resulted in the long hydrophobic chain shrinkage of P123 [56], giving rise to the network shrinkage of AgSBA-15. Silver metal has major diffraction peaks at  $2\theta = 38^\circ$ ,  $44.2^\circ$ ,  $64.4^\circ$ , and  $77.6^\circ$ , corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) lattice planes of the cubic structure of Ag, which are clearly found in the wide-angle X-ray diffraction data ( $2\theta = 35\text{--}80^\circ$ ) of AgSBA-15 (Fig. 2), confirming the formation of crystalline silver.

Fig. 3 shows the X-ray photoelectron spectrum of AgSBA-15 in the Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub>. The Ag 3d<sub>5/2</sub> peak is centered at 368.23 eV. This binding energy matches well with that of Ag(0) 3d<sub>5/2</sub> [57] and no obvious peak of Ag<sup>+</sup> is observed, which indicates that the silver element has been totally reduced and confined on the surface of the SBA-15.

As shown in Fig. 4, the TEM images of AgSBA-15 show hexagonal array of mesoporous channels, as indicated by the above SAXRD

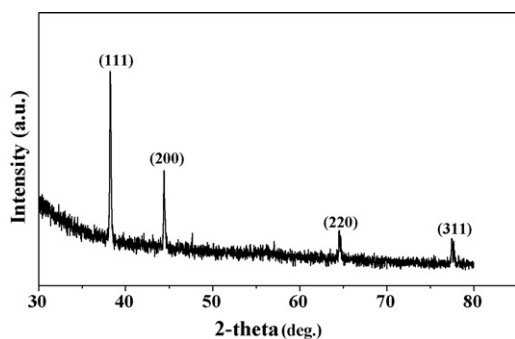


Fig. 2. Wide-angle XRD pattern of calcined AgSBA-15 sample.

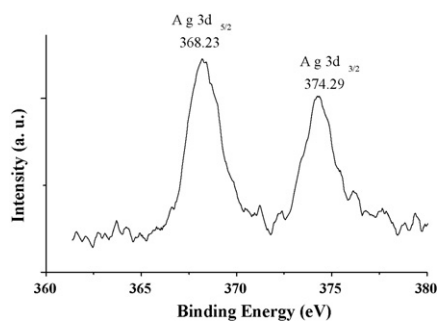


Fig. 3. XPS spectrum of AgSBA-15 sample.

result. Although some silver ions were reduced on the outer surface of the SBA-15, no bulk aggregation of the metal can be found. The uniform dispersion of Ag-nanoparticles on the inner surface and on the outer surface of AgSBA-15 channels can be clearly observed. The existence of the Ag-nanoparticles can be further proved by energy dispersive spectroscopy analysis of X-rays (EDAX).

Fig. 5 shows the nitrogen adsorption and desorption isotherms of SBA-15 and AgSBA-15. Type IV isotherm curves with a well-defined step clearly indicate that these materials possess a mesoporous structure with cylindrical channels. Three well-distinguished regions of the adsorption isotherms are obvious: (1) monolayer multilayer adsorption ( $P/P_0 = 0-0.5$ ); (2) capillary condensation ( $P/P_0 = 0.5-0.8$ ) and (3) multilayer adsorption on the outer surface ( $P/P_0 = 0.8-1.0$ ). A sharp inflection in the relative pressure ( $P/P_0$ ) between 0.5 and 0.8 corresponds to capillary condensation within uniform mesopores, and is a function of the pore

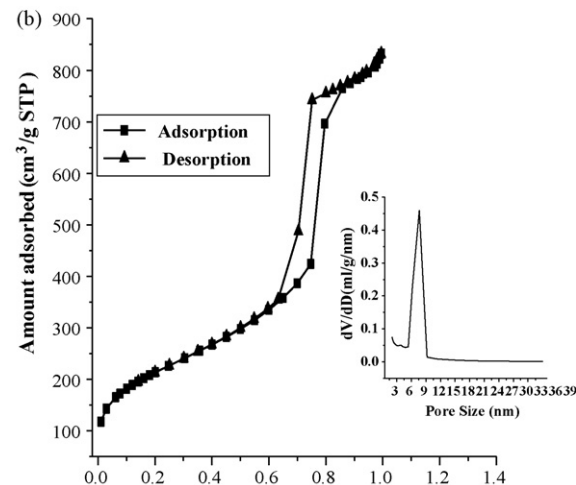
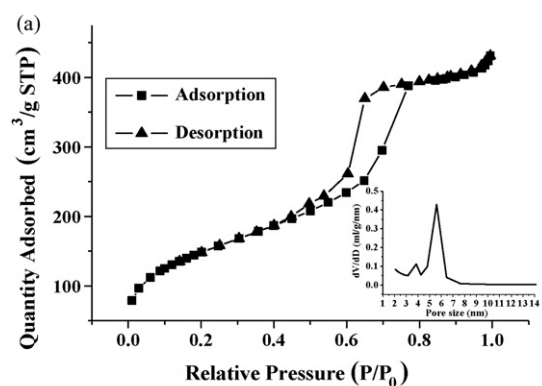


Fig. 5. The nitrogen adsorption and desorption isotherms and pore size distribution curves (insets) for AgSBA-15 (a) and SBA-15 (b) samples.

diameter. The uniform pore size distribution is demonstrated by the sharpness of this step and displayed in the insets of Fig. 5a and b. The decreases of the BET surface area, BJH pore volume and average pore size together with the increased thickness of the pore wall, can be attributed to the incorporation of Ag-nanoparticles on SBA-15. However, the BET surface area of AgSBA-15 ( $525 \text{ m}^2 \text{ g}^{-1}$ ) is lower than SBA-15 ( $773 \text{ m}^2 \text{ g}^{-1}$ ), which can be attributed to the agglomeration of Ag-nanoparticles that partly block the pore space of mesoporous channels.

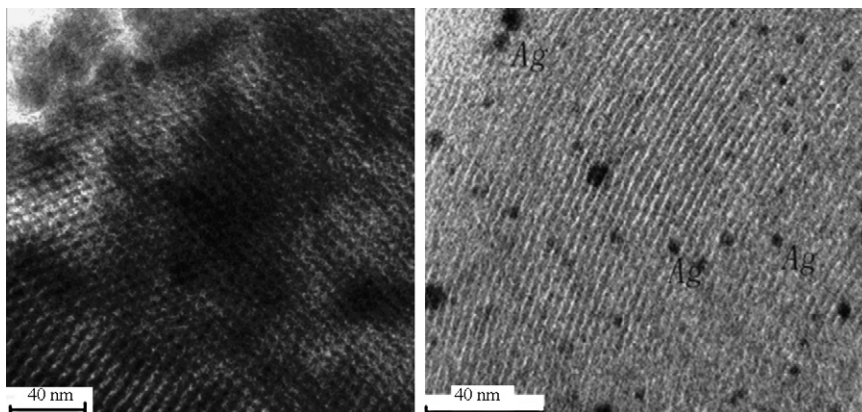
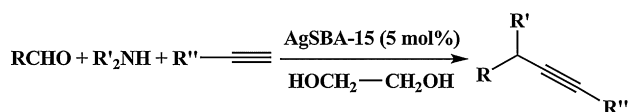


Fig. 4. TEM images of the AgSBA-15 catalyst viewed along (left) [001] and (right) [100] directions.

**Scheme 1.** Three-component synthesis of propargylamines catalyzed by AgSBA-15.**Table 1**Effect of solvents on the A<sup>3</sup>-coupling reaction using AgSBA-15-6 as catalyst<sup>a</sup>.

Run	Solvent	Yield <sup>b</sup> (%)
1	CH <sub>2</sub> Cl <sub>2</sub>	0
2	CHCl <sub>3</sub>	0
3	Toluene	42
4	CH <sub>3</sub> OH	48
5	CH <sub>3</sub> CN	65
6	H <sub>2</sub> O	Trace
7	Glycol	73

<sup>a</sup> Reaction conditions: butaldehyde (1.0 mmol), diethylamine (1.2 mmol), phenylacetylene (1.5 mmol), AgSBA-15-6 (5 mol%), solvent (5 ml), nitrogen, 100 °C, 2 h.<sup>b</sup> Isolated yields.**Table 2**Recycling of the catalytic system for the A<sup>3</sup>-coupling reaction<sup>a</sup>.

	Run				
	1	2	3	4	5
Yield <sup>b</sup> (%)	73.4	72.8	71.5	68.0	26.2

<sup>a</sup> Reaction conditions: butaldehyde (1.0 mmol), diethylamine (1.2 mmol), phenylacetylene (1.5 mmol), AgSBA-15-6 (5 mol%), glycol (5 ml), nitrogen, 100 °C, 2 h.<sup>b</sup> Isolated yields.

### 3.2. Catalytic studies

Our initial investigation focused on the effect of solvents on the A<sup>3</sup>-coupling reactions of butaldehyde, phenylacetylene, and diethylamine (Scheme 1). In general, A<sup>3</sup>-coupling reactions were carried out in toluene, CH<sub>3</sub>CN, THF, and other solvents. Here, different solvents were employed in the A<sup>3</sup>-coupling using AgSBA-15-6 as catalyst at 100 °C, and the results are summarized in Table 1. From Table 1, it is evident that glycol and CH<sub>3</sub>CN are suitable reaction solvents for A<sup>3</sup>-coupling reaction (runs 5 and 7), whereas toluene and CH<sub>3</sub>OH afforded lower yields (runs 3 and 4). No or trace products were obtained when the reactions were carried out in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> or H<sub>2</sub>O. Although the polar solvents, such as glycol or CH<sub>3</sub>CN afforded good yields, when water was used as the solvent, only a trace amount of product was observed even after a prolonged reaction time. To avoid the use of volatile solvents and

**Table 4**A<sup>3</sup>-coupling of aldehydes, alkynes and secondary amines<sup>a</sup>.

Run	Aldehydes	Alkynes	Amines	Time (min)	Yield <sup>b</sup> (%)
1	Paraformaldehyde	Phenylacetylene	Diethylamine	30	95.0
2	Butaldehyde	Phenylacetylene	Diethylamine	120	73.4
3	Pentanal	Phenylacetylene	Diethylamine	240	68.0
4	Heptaldehyde	Phenylacetylene	Diethylamine	240	52.0
5	Paraformaldehyde	Phenylacetylene	Piperidine	30	95.0
6	Butaldehyde	Phenylacetylene	Piperidine	120	61.0
7	Pentanal	Phenylacetylene	Piperidine	240	53.2
8	Heptaldehyde	Phenylacetylene	Piperidine	240	42.8
9	Paraformaldehyde	Hex-1-yne	Diethylamine	30	86.0
10	Butaldehyde	Hex-1-yne	Diethylamine	120	68.0
11	Heptaldehyde	Hex-1-yne	Diethylamine	240	50.0
12	Paraformaldehyde	Hex-1-yne	Piperidine	30	80.0
13	Butaldehyde	Hex-1-yne	Piperidine	120	57.0
14	Heptaldehyde	Hex-1-yne	Piperidine	240	40.0

<sup>a</sup> Reaction conditions: aldehydes (1.0 mmol), secondary amines (1.2 mmol), alkynes (1.5 mmol), AgSBA-15-6 (5 mol%), glycol (5 ml), nitrogen, 100 °C (for paraformaldehyde 75 °C).<sup>b</sup> Isolated yields.**Table 3**Effect of Ag-nanoparticle size on A<sup>3</sup>-coupling reaction<sup>a</sup>.

Catalyst	Ag content <sup>b</sup> (%)	Particle size <sup>c</sup> (nm)	Yield <sup>d</sup> (%)	
			Butaldehyde	Pentanal
SBA-15	0		0	0
AgSBA-15-1	0.26	4-5	35.0	28.1
AgSBA-15-2	0.42	4-5	37.1	28.6
	<u>6.78</u>	<u>4-5</u>	<u>56.4</u>	<u>49.3</u>
AgSBA-15-3	3.23	8	46.2	44.9
AgSBA-15-4	5.28	8	61.0	59.7
AgSBA-15-5	5.89	8	65.3	61.3
AgSBA-15-6	<u>6.86</u>	<u>8</u>	<u>73.4</u>	<u>68.0</u>
AgSBA-15-7	10.62	12	66.0	56.4
AgSBA-15-8	20.03	33	44.0	42.2
AgSBA-15-9	32.15	40	30.1	28.0
AgSBA-15-10	49.72	41	26.2	22.6

The underlines emphasize catalysts with similar Ag content but different particle sizes exhibit different yields.

<sup>a</sup> Reaction conditions: aldehydes (1.0 mmol), diethylamine (1.2 mmol), phenylacetylene (1.5 mmol), catalysts (5 mol%), glycol (5 ml), nitrogen, 100 °C.<sup>b</sup> Determined by ICP.<sup>c</sup> Estimated by the Scherrer equation from XRD patterns.<sup>d</sup> Isolated yields.

to reduce the environmental pollution, all the three-component coupling reactions were performed with glycol as “green” solvent.

Heterogeneous catalysts offer ease of handling and purification through simple filtration. They also allow catalyst recovery and recycling, another interesting eco-friendly aspect of these catalysts. In order to examine this possibility, we carried out the A<sup>3</sup>-coupling reaction several times with the same AgSBA-15-6 catalyst under the same condition. Before reuse, the solid was separated from the reaction medium by filtration, washed with dichloromethane and finally dried at 40 °C. The reaction yield (Table 2) shows that AgSBA-15-6 catalyst can be repeatedly used four times without apparent decrease in its catalytic activity. At the same time, the Ag content in the fresh and used catalyst after 4 cycles was found to be similar (Ag in the fresh catalyst: 6.86%, and in the used catalyst after 4 cycles: 6.50%, analyzed by ICP). These studies clearly demonstrate that the silver is strongly bonded onto the silica surface during the reaction.

A series of experiments were carried out in an effort to investigate catalytic action of Ag-nanoparticles with different sizes and the results are presented in Table 3. Ag-nanoparticles with different sizes, ranging from about 4–5 to 41 nm (estimated by the Scherrer equation from XRD patterns), were prepared using various AgNO<sub>3</sub> amounts during preparation procedure. The study shows that the

catalytic action is dependent on the Ag-nanoparticles size (Table 3). The maximum reaction yield has been observed for an average Ag-nanoparticle size of about 8 nm, because Ag-nanoparticles with average size of 7 nm show more excellent catalytic activity [58]. With a decrease in particle size, a trend of decreasing reaction yield has been found for Ag-nanoparticle size of less than 8 nm, even if the catalytic amount of AgSBA-15-2 catalyst (particle size ~4–5 nm) was increased in order to make Ag content up to 6.78%, which was similar to the Ag content (6.86%) of AgSBA-15-6 catalyst (particle size ~8 nm). Furthermore, those above 8 nm also show a steady decline of reaction yield with increasing Ag-nanoparticles size. It has been postulated that in the case of particles of average size less than 8 nm, a downward shift of the Fermi level takes place, with a consequent increase of band gap energy. As a result, the particles require more energy to pump electrons to the adsorbed ions for electron transfer reaction [44]. This leads to a reduction in reaction yield when catalyzed by smaller particles. As for Ag-nanoparticles larger than 8 nm, the decrease in catalytic efficiency could be ascribed to less adsorption surface area with increasing particle size. From Table 3, it is also found that with similar Ag-nanoparticles size (AgSBA-15-3–AgSBA-15-6), the reaction yield increases with increasing Ag content.

With above conditions in hand, we then explored the scope of this AgSBA-15-catalyzed  $A^3$ -coupling reaction (Table 4). The effect of the aldehydes with various aliphatic chain lengths was examined. According to the steric hindrance, the longer aliphatic chain, the more difficult reaction, and the reverse should also be true. When increasing the steric hindrance of aldehydes (runs 3 and 4), it consumed longer time to complete the reaction and gave a decrease in yield. The effect of the amine was also examined, and it was found that cyclic secondary amine, piperidine, gave similar results to diethylamine in terms of reaction time, except that yield were lowered, which may also be consequence of steric hindrance. As a result, the reaction was found to be highly affected by the steric hindrance of the aldehydes, which is probably ascribed to the limitation effect of the SBA-15 channels that strongly influence the addition of iminium ions to activated alkynes. This hypothesis is consistent with our result that aromatic aldehydes could only afford trace or even no products.

#### 4. Conclusions

In summary, a new heterogeneous catalyst system, AgSBA-15, has been successfully prepared by an in situ reduction method using HMTA as mild and efficient reducing agent, which can catalyze  $A^3$ -coupling reaction in more environmentally friendly medium with glycol as a “green” solvent. It is also found that the maximum reaction yield has been achieved for an average Ag-nanoparticle size of about 8 nm. Furthermore, the catalyst can be readily recovered and reused for several cycles with only a slight decrease in catalytic activity.

#### Acknowledgements

This work was financially supported by National Nature Science Foundation of China (Grant No. 20872135) and China National Tobacco Corporation (110200701007).

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.03.007.

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