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Silica/chitosan core-shell hybrid-microsphere-

supported CuI catalyst for terminal alkyne

homocoupling reaction

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Graphical abstract



Highlights

- Silica/chitosan core-shell hybrid microspheres were prepared in microchannel.
- These hybrid microspheres have controlled structure and component distribution.
- As catalyst support for fast reaction, they could reduce mass transfer resistance.
- The reaction could complete within 10min without solvent at room temperature.
- It's easy to recover and reuse the supported catalyst with high catalytic activity.

Abstract: A new microfluidic approach to prepare silica/chitosan core-shell hybrid microspheres was developed. The hybrid microspheres exhibit improved mechanics and adsorption properties. In addition, the silica/chitosan-supported CuI is an outstanding catalyst for terminal alkyne homocoupling reaction. Because there is chitosan with a large amount of –NH₂, which has a strong force with metal ions, on the shell of the microspheres, the chitosan can effectively reduce mass transfer resistance. Meantime, the chitosan can adsorb reactants and subsequently increase the reactant concentration around the catalyst. These two reasons make this solvent-free reaction complete within 10 min at room temperature. It is easy to recover the catalyst simply through sedimentation by centrifuge. Furthermore, the silica/chitosan-supported catalyst can be reused many times with high catalytic activity.

Keywords: silica-chitosan hybrid microspheres; core-shell; supported catalyst; Glaser coupling; microfluidic

1. Introduction

With the increasing consciousness of environmental protection, it is increasingly important to perform chemical reactions under benign conditions with recyclable catalysts. Catalysts are usually immobilized on a solid, green support for easy separation and reuse. To a large extent, catalytic activities depend on the properties of the supports; therefore, the development of better catalyst supports is necessary. To date, different support materials have been reported, including inorganic materials (e.g., SiO₂, [1, 2] Al₂O₃, [3] zeolites [4]) and organic materials (e.g., polystyrenes, polysaccharides). It has been demonstrated that support properties, which include the material itself and the structure, play an important role in the catalyst's performance. Ji et al. [3] found apparent differences in the decomposition and reduction processes between unsupported and Al₂O₃-supported metal compounds only because of their different existing states. In Bouilhac's work, [5] the catalyst that was bound to a star-like polystyrene composed of a microgel core with functionalized arms showed high catalytic activities, and this special support structure contributed to the polystyrene's monomodal molar mass distribution. It is essential to choose suitable support materials with optimized structures for specific chemical reactions.

1,3-Diyne derivatives, which are intermediates, play an important role in the preparation of various structural entities, particularly macrocyclic annulenes, organic conductors, supramolecular switches and carbon-rich materials. Terminal alkyne homocoupling reactions, which are also known as Glaser coupling, are notably important in the preparation of 1,3-diynes. [6-10] The reaction is usually performed with Cu or Pd as the catalyst and organic base under heated condition in organic solvents, which are not environmentally friendly. [11-15] An environmentally friendly, efficient and solvent-free method for the terminal alkyne homocoupling reaction was reported in 2010. [7] The terminal alkyne can be totally transformed at 60° C after 6 h with catalytic amounts

of Cu(II) salt and base. The catalyst can also be recycled. However, the relatively high temperature and long reaction time must be improved. He et al. [16] developed a benign, solvent-free method to transform terminal alkyne to 1,3-diynes at room temperature by loading the copper catalyst on Amberlyst A-21. However, considerably more attention has been paid to the support material properties and less to the structural properties, which are also important to the catalyst's performance. For example, the catalyst inside the support cannot be efficiently used. Thus, the core-shell supported catalyst with the catalyst on the shell is beneficial to take full advantage of the catalyst and obtain high yield in a short time. [5] Lin et al. [17] prepared the Pd/SiO₂@ZIF-8 core-shell catalyst and used it in the hydrogenations of alkenes. This core-shell catalyst exhibits selective, antipoisoning and antileaching properties. Therefore, it is important to develop a simple method to prepare the support with a core-shell structure to investigate the effect of the support structure on terminal alkyne homocoupling reactions.

Chitosan, which is the only basic polysaccharide in nature, is abundant. Chitosan has outstanding properties, such as nontoxicity, biocompatibility, biodegradability and low cost. Chitosan has a large amount of amino and hydroxyl groups, which have strong chelating characteristics with metal ions and organics. [18] Furthermore, chitosan's good formability enables convenient structure regulation. However, the poor mechanical property restricts its practical applications. Recently, chitosan was composited with inorganic materials because the obtained hybrid material showed improved catalytic, thermal and mechanical properties through synergistic effects. [19-22] Therefore, hybrid materials have been applied in diverse fields, such as catalysis, separation techniques, smart coating, and immobilization of enzymes.

It has been demonstrated that silica-chitosan hybrid materials exhibit an enhanced mechanical property compared with other hybrid materials. [19, 20] In addition, silica has superior

biocompatibility, insolubility, mechanical stability and adsorption properties. Thus, the silica/chitosan hybrid material is a good candidate for catalyst support. The primary preparation approach of core-shell hybrid microspheres is the layer-by-layer technique using electrostatic force. [23, 24] Although obtaining core-shell hybrid microspheres is relatively easy, regulating the structure and repeating the process are difficult. Therefore, an easy approach to prepare silica/chitosan core-shell hybrid microspheres with controllable structures and better repeatability is essential.

In the past decade, microfluidic technology has rapidly developed and shows great advantages in synthesizing monodispersed microspheres with different structures. [25-27] Many microfluidic devices have been developed for high-throughput production. [28] In our previous work, chitosan/silica core-shell hybrid microspheres with silica shell and chitosan core were prepared as a catalyst support with most catalysts in the core for a slow reaction. Compared with other microspheres, chitosan/silica core-shell hybrid microspheres have higher catalyst load efficiency; therefore, a higher yield was obtained in mild condition in the azide-alkyne cycloaddition reaction, which was controlled by a reaction instead of mass transfer. However, this approach could not satisfy the demands of fast reactions because the mass transfer path was too long. To develop a suitable catalyst support for a fast reaction that is controlled by reaction itself, we developed a facile microfluidic approach to prepare silica/chitosan core-shell hybrid microspheres with silica core and chitosan shell in this work. Silica/chitosan-supported CuI was used as a green catalyst for the terminal alkyne homocoupling reaction without any solvent at room temperature. The silica/chitosan core-shell hybrid support can decrease the mass transfer resistance and effectively adsorb terminal alkyne, which leads to a short reaction time. Furthermore, the supported catalyst has good stability and is recyclable.

2. Experimental

2.1 Materials and chemicals

Chitosan (0.20 g, deacetylation degree below 95%, Sinopharm chemical reagent Co., Ltd., Beijing, P.R. China) aqueous solution with acetic acid (0.20 g, VAS Chemical Co., Ltd., Tianjin, P.R. China) was used as the middle fluid. A certain amount $(1.0 \sim 4.0 \text{ g})$ of tetraethoxysilane (TEOS) was dissolved in the acetic acid (0.20 g) aqueous solution and stirred overnight to prepare a silica sol (10.0 g), which was used as the inner fluid. N-octanol (VAS Chemical Co., Ltd., Tianjin, P.R. China) served as the continuous phase. N-octane (10.0 g) with cross-linking reagent, glutaraldehyde, (0.040 g) and surfactant, Span 80, (0.20 g, VAS Chemical Co., Ltd., Tianjin, P.R. China) was used as the solidification bath. N-butylamine (0.5 mmol, VAS Chemical Co., Ltd., Tianjin, P.R. Tianjin, P.R. China), CuI and phenyl acetylene (1.0 mmol, Alfa Aesar, Tianjin, P.R. China) were used in the catalysis reaction.

2.2 Microfluidic device

The microfluidic device was described in details in our previous work. [29] A circular glass capillary (0.3 mm \times 0.6 mm) is tapered to approximately 20 µm using a micropipet puller (P-97, SUTTER Co. Ltd., USA) for the inner fluid. This device is inserted into a second glass capillary (1.05 mm \times 1.5 mm), the orifice of which is tapered to approximately 150 µm for the middle fluid. Next, the orifices of those two compound capillaries are inserted into a Teflon tube with 0.5 mm inner diameter, as shown in Fig. 1. The Teflon tube is inserted as the continuous phase inlet and the multiphase flow's channel to form the co-axial structure. [29] These fluids are pumped into the microchannel through three microsyringe pumps and four gastight microsyringes. The droplets are collected with a solidification bath, which is placed on a shaker.

2.3 Preparation of monodispersed silica/chitosan core-shell hybrid microspheres with different structures

To prepare silica/chitosan core-shell hybrid microspheres, the inner and middle fluids were injected into the microchannel and broken into monodispersed droplets by the shearing force of the continuous flow at the intersection. The droplets were collected in the solidification bath, where the Schiff's base reaction between glutaraldehyde and chitosan and the extraction of water out of droplets using n-octanol were used to pre-solidify the droplets. The microspheres' structure depends on the pre-solidification time, which could be controlled by adjusting the residence time in the solidification bath. Then, the microspheres were washed with and submerged in n-octane for 24 h to ensure the silica gelation. Finally, the spheres were dried by freeze-drying.

The silica-chitosan hybrid microspheres with uniform component distribution, which are called homogeneous hybrid microspheres in the following text, were also prepared as the control group. The operation was described in details in our previous work. [20] The amount of TEOS and chitosan in the homogeneous hybrid microspheres were identical to that in the core-shell hybrid microspheres.

2.4 Adsorption kinetics experiments of Cu(II)

First, 0.030 g microspheres were added into a conical flask, which was placed in a water-bath shaker at 30 °C and 130 rpm with 25 ml aqueous solution of 100 ppm Cu(II). A Raman atomic absorption spectrophotometer (Type Z-5000, Hitachi, Japan) was used to analyze the Cu(II) concentration of the sample solution, which was taken out at fixed time intervals. Based on the mass balance equation, the amount of adsorbed Cu(II) per unit weight of the microspheres at time ti, which is denoted by q(ti) (mg/g), was calculated as:

$$q(t_i) = \frac{C_0 V_0 - \sum_{1}^{i-1} C_i V - C_i [V_0 - (i-1)V]}{m}$$

where C_0 (mg/l) is the initial Cu(II) concentration, C_i is the concentration at time t, V is the volume of the remaining solution at time ti (samples that were taken out were not added back to the beaker), and m is the weight of the microspheres in the beaker.

2.5 Preparation of hybrid-microsphere-supported copper catalyst

In a nitrogen atmosphere, a conical flask with different amounts of hybrid microspheres, CuI (0.20 g) and CH₃CN (10 ml) was put into a water-bath shaker at room temperature for 24 h. Next, the resulting microspheres were separated, washed with CH₃CN and CH₂Cl₂, and dried in vacuum overnight.

2.6 Catalysis of the terminal alkyne homocoupling reaction

A certain amount of the supported catalyst, phenylacetylene and n-butylamine was added into a conical flask. The reaction was performed at room temperature for 10~35 min. Finally, the product of 1,4-diphenylbutadiyne was separated by dissolving in CH₂Cl₂ and purified by recrystallization or column chromatography. Dividing the weight of obtained product by the weight calculated in theory, the yield can be obtained. Dividing the weight of phenylacetylene converted to product by its initial weight, the conversion can be obtained. The space-time yield (STY) was defined as the weight of product obtained per gram of supported catalyst in one hour. Normalized yield was used in the reactant ratio optimization experiment. Divide the yield obtained under different reactant ratio by the maximum yield, then the normalized yield could be obtained. The ratio of phenylacetylene to n-butylamine was abbreviated as alkyne : amine. The catalyst was simply separated by sedimentation and subsequently reused after dried.

The reaction was also performed with the unsupported CuI in an identical procedure as above, except that the catalyst was separated by centrifuge.

2.7 Adsorption of phenylacetylene

An n-octanol solution of phenylacetylene with an initial concentration of 402.6 mg/ml was obtained by mixing a certain amount of phenylacetylene with n-octanol. Next, 0.30 g microspheres were added into 10 ml solution and placed in a water-bath shaker at 30°C and 130 rpm. A fixed volume of the solution was taken out after 10 min and 20 min and analyzed with gas chromatography-mass spectrum (GC-MS, ISQ) to obtain the concentration of phenylacetylene to find the phenylacetylene adsorption capacity of the hybrid microspheres.

2.8 Analysis and characterization

The preparation process and overall morphology of the droplets and microspheres were observed using an optical microscope (Type BX-61, Olympus, Japan) and an on-line CCD (Pixelink, Canada). The detailed structure of the microspheres and element analysis were obtained with scanning electron microscopy (SEM, type TM3000 and F6301, Hitachi, Japan). The element valence of the catalyst was obtained using x-ray photoelectron spectroscopy (XPS) in a PHI Quantera SXM system (ULVAC-PHI Inc., Kanagawa, Japan) with a monochromatic Al KR source and a charge neutralizer. The product was analyzed by Fourier transform infrared spectroscopy (Type Tensor27, Bruker, Germany) and gas chromatography-mass spectrum (GC-MS, ISQ).

3. Results and Discussion

3.1 Formation and characterization of the silica/chitosan core-shell hybrid microspheres

The inner and middle fluids broke up into droplets because of the shearing force of the continuous phase at the intersection of the microchannel, as shown in Fig. 1. In the solidification bath, the droplets were pre-solidified through Schiff's base reaction between chitosan and glutaraldehyde and the extraction of water from the droplets by n-octanol. After the 24 h gelation in n-octane, silica/chitosan core-shell hybrid microspheres were obtained. The pre-solidification bath and n-octane.

The typical silica/chitosan core-shell hybrid microspheres (2.0 wt. % TEOS in the inner fluid and 2.0 wt. % chitosan in the middle fluid, pre-solidified for 20 min and gelated for 24 h) were used to characterize the component distribution and core-shell structures. It was observed that the droplets had good sphericity and a uniform size distribution in Fig. 2 a. The energy spectrum results in Fig. 2 b demonstrate that the silica was successfully composited in the microspheres. Next, to ensure the core-shell structure of the hybrid microspheres, the spheres that were calcinated at 800°C or washed in the alkaline solution were compared to the original ones, as shown in Figs. 2 c, d and e. The diameter of the microspheres after calcination significantly decreased because of the loss of the chitosan shell. The microspheres that were washed in the alkaline solution had only the shell and a nearly hollow core because of the loss of silica. This result proves that the hybrid microspheres have a core-shell structure with a silica core and a chitosan shell. It should be noted that the usual core-shell microspheres are composed of two immiscible materials. Then, there is a clear dividing line between the core and the shell. In this work, the inner fluid (silica sol) and the middle fluid (chitosan aqueous solution) are miscible. Although they are injected through different

channels, there will be mass transfer when they form the droplets and contact each other. Furthermore, the distribution of chitosan and silica in different types of hybrid microspheres can be calculated according to the energy spectrum results because there is C only in chitosan and Si

 $\frac{Si_{out}}{Si_m} \sum_{C_{out}} Si_m \sum_{$

The hybrid microspheres show a core-shell structure in terms of component distribution at the micro-scale. The macro-scale structures of the hybrid microspheres can also be adjusted by changing the pre-solidification time for the identical gelation time of 24 h, as shown in Fig. 3. The structure changed from completely porous to a compact shell and a porous core and subsequently to completely compact with the increase in pre-solidification time, as shown in Figs. 3 a-j. The diffusion of glutaraldehyde from outside to inside the microspheres made the microspheres gradually become compact from the outside. Simultaneously, the water inside microspheres was extracted outside by n-octanol, which also contributed to the compact structure.

3.2 Adsorption and catalytic properties of the core-shell hybrid microspheres as support

Because the load efficiency of the catalyst on the support significantly affects the catalytic activity, the adsorption properties of the hybrid microspheres were studied. Fig. 4 a shows the adsorption of Cu(II) by the microspheres with different amounts of pre-solidification time. A larger adsorption

amount could be obtained with shorter pre-solidification time because the free $-NH_2$ amount determines the adsorption amount. Longer pre-solidification time implies that much more $-NH_2$ is consumed in the Schiff's base reaction. The effect of the TEOS-to-chitosan ratio on adsorption was also studied for the identical pre-solidification time of 20 min, as shown in Fig. 4 b. In the experimental range, the adsorption amount slightly decreased with the increasing ratio possibly because more silica hindered the exposure of $-NH_2$. However, the effect was small, and a larger amount of silica increased the mechanical intensity, which indicates that it could withstand a considerably larger force. Therefore, 2% TEOS was used in the experiment. Then, the adsorption amount can change in a larger range by preparing silica/chitosan core-shell microspheres.

However, as the catalyst support, whether there is an optimized catalyst-loading amount for the reaction requires further study, as shown in Fig. 5. The space-time yield and yield in 30 min both increased at first and subsequently decreased when the load ratio increased, but they did not simultaneously reach the maximum. The optimized load ratio of the yield was larger than that of the space-time yield because when the load ratio was small, they would increase with the catalytic site increasing. However, when the load ratio reached a certain value, although the yield continued to increase, the space-time yield began to decrease because of the inhibition effect among the catalytic sites. Not all catalytic sites could participate when the load ratio was too large; thus, they both decreased. For a better catalytic effect, the load ratio of the highest yield was used in the catalytic reaction.

Compared with homogeneous hybrid microspheres, we must investigate whether core-shell hybrid microspheres as the support have advantages in the catalysis of fast reactions, such as the terminal alkyne homocoupling reaction. The two types of microspheres were compared with each other under the same experiment conditions. To study the reaction clearly, a less supported catalyst

was used to slow the reaction, and the results are shown in Fig. 6. The kinetic equations for coreshell hybrid microspheres and homogeneous hybrid microspheres are equations (1) and (2), respectively.

$$y = -0.0012x^{2} + 0.0752x - 0.2832$$
 (1)

$$y=0.0198x+0.1157$$
 (2)

Higher yield was obtained for the identical reaction time using the core-shell-microspheresupported catalyst. According to the equation

$$-\frac{dC_A}{dt} = kC_A^{\alpha} \tag{3}$$

where α is the reaction order for the reactant, the two curves were calculated, and α was 1.56 and 0 for the core-shell hybrid microspheres and homogeneous ones, respectively. Thus, the reaction was controlled by mass transfer when homogeneous hybrid microspheres were used as the support. When core-shell hybrid microspheres were used as the support, the mass transfer resistance was reduced because the catalyst was distributed on the microsphere surface, and a higher yield was consequently obtained in a shorter time. Therefore, as the catalyst support, the silica/chitosan coreshell hybrid microspheres are beneficial for the solvent-free terminal alkyne homocoupling reaction.

Next, the catalytic performance of silica/chitosan core-shell hybrid-microsphere-supported catalyst was further optimized. The effect of the catalyst amount on the yield was studied at the fixed reaction time of 10 min and fixed reactant amounts (0.450 mmol alkyne and 0.225 mmol amine without any solvent), as shown in Fig. 7. The relationship between the yield and supported catalyst weight is as follows:

$$y=0.0603x-0.1332$$
 (4)

Higher yield could be obtained with the increase in amount of the supported catalyst, and they were linearly related, which indicates that the reaction order for the catalyst was 1. When the catalyst amount was 17.0 mg, the reaction finished within 10 min.

The reactant ratio should also be optimized after optimizing the effect of the amount of supported catalyst on the reaction to avoid pollution and waste caused by excess reactants for this solvent-free reaction. The amount of added n-butylamine should be considered because it was required in the reaction. The yields of product under different reactant ratios were obtained. Normalized yield was used here. And normalized yield means yields obtained under different reactant ratio divides by the maximum yield. The highest yield was obtained when the alkyne-to-amine (phenylacetylene : n-butylamine) ratio was 0.4, as shown in Fig. 8, because low concentrations of phenylacetylene and n-butylamine decrease the reaction rate. Therefore, there is an optimal ratio.

The experimental conditions were optimized, and the reaction completed within 10 min under the optimized conditions, which was relatively faster. Table S2 shows that the hybrid microspheres can effectively adsorb phenylacetylene because large amounts of $-NH_2$ and -OH, which are strong electron donors, can have relatively strong interactions with phenylacetylene, which is an electron acceptor. Thus, the concentration of phenylacetylene around the supported catalyst increases, and the reaction rate increases, which is another reason for the better catalytic performance.

3.3 Study of the catalytic stability of silica/chitosan core-shell hybrid microspheres as catalyst supports

Based on the optimized catalyst amount and experimental conditions, the catalytic stability of silica/chitosan core-shell hybrid-microsphere-supported catalyst was also studied. The supported catalyst was recycled, and the results are shown in Table 2. High yield was obtained in a short time, and the supported catalyst could be reused for more than 5 times. Due to 1,4diphenylbutadiyne is the only product in this condition, therefore the conversion of reactant is equal to yield. The catalyst had good stability and maintained good catalysis performance even after a few days. CuI is relatively stable in dry condition, but it becomes inactive when it contacts water in the reaction process because the reaction is exposed in the air, and a small amount of water enters with the reactants. The results were compared with other works and exhibit good catalytic performance, as shown in Table S3. However, the performance certainly decreased after 5 times of usage, and the reason was investigated. The reason is not the loss of Cu but the conversion of CuI to Cu₂O, CuO and Cu(OH)₂, as shown in Tables 3 and S1. It could be found that the supported catalysts could keep the valance of Cu as well as the unsupported ones. However, the unsupported catalysts couldn't be collected and recycled effectively and most were lost and became pollutant. The XPS results in Fig. S1 show that the inactive catalyst had two peaks, which implies that a part of Cu(I) was converted to other formations, whereas the fresh catalyst had only one peak. Thus, the silica/chitosan core-shell microspheres had a strong interaction with the catalyst and could avoid the loss of catalyst. In addition, the support enabled the catalyst's easy recycling and prevented its agglomeration.

4. Conclusions

Silica/chitosan core-shell hybrid microspheres with different structures and component distributions were prepared using a facile microfluidic method. The hybrid microspheres exhibit good adsorption property of heavy metal ions, such as Cu(II). The effects of the pre-solidification

time and TEOS content in the inner fluid on the structure and adsorption performance of the hybrid microspheres were systematically studied. The optimized experimental conditions for the porous core-shell hybrid microspheres are 2.0% chitosan in the middle fluid, 2.0% TEOS in the inner fluid and pre-solidification time of 20 min. The hybrid-microsphere-supported CuI also shows outstanding catalytic activity in the solvent-free terminal alkyne homocoupling reaction. Compared with homogeneous hybrid microspheres, the silica/chitosan core-shell hybrid-microsphere-supported catalyst can effectively decrease the mass transfer resistance; meanwhile, the silica/chitosan hybrid microspheres can adsorb terminal alkyne, which leads to a higher reactant concentration around the catalyst and consequently increases the catalytic reaction speed. The reaction order of the supported catalyst is 1, and with a suitable amount of catalyst, the reaction can finish within 10 min at room temperature without any solvent. The entire process is relatively green. Furthermore, the supported catalyst has good stability with relatively high catalytic performance for more than 5 times without losing its activity.

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Figure captions Fig. 1. The schematic diagram of microfluidic device [29]

Fig. 2. (a) Optical micrographs of silica/chitosan hybrid microspheres; (b) Results of the energy spectrum of silica/chitosan hybrid microspheres; (c) SEM images of silica/chitosan hybrid microspheres without any treatment (the scale bar is 200 μ m); (d) SEM images of silica/chitosan hybrid microspheres after calcination under 800°C (the scale bar is 100 μ m); (e) SEM images of silica/chitosan hybrid microspheres that were washed by an alkaline solution (the scale bar is 200 μ m).

Fig. 3. SEM images of the surface and inner region of the hybrid microspheres with different presolidification time of 20, 30 and 40min. (a), (c), (e), (g) and (i) are the images of integral microspheres with pre-solidification time of 10 min, 20 min, 45 min, 60 min and 90 min, respectively. (b), (d), (f), (h) and (j) are the images of broken microspheres with pre-solidification time of 10 min, 20 min, 45 min, 60 min and 90 min, respectively.

Fig. 4. Adsorption properties. (a) Adsorption kinetic curves of Cu by hybrid microspheres with different pre-solidification time; (b) Effect of the TEOS ratio in the dispersed phase on the equilibrium adsorption amount of Cu by hybrid microspheres (initial concentration of Cu is 100ppm, pre-solidified for 20 min).

Fig. 5. Relationship between load ratio of Cu on support and yield or space-time yield (STY). Reaction conditions: phenylacetylene (1.0 mmol); n-butylamine (0.5 mmol); room temperature in air; reaction time (30 min)

Fig. 6. Catalytic performance of silica-chitosan core-shell or homogeneous hybrid microspheres supported CuI. (Reaction conditions: phenylacetylene (1.0 mmol); n-butylamine (0.4 mmol); Cat. (2.2 mol% of the copper content); room temperature in air).

Fig. 7. Effect of weight of supported catalyst (hybrid microspheres loaded with CuI) on the reaction yield. (Reaction conditions: phenylacetylene (0.450 mmol); n-butylamine (0.225 mmol); room temperature in air; reaction time (10 min)).

Fig. 8. Effect of the alkyne-to-amine ratio on the reaction yield (the yield here represents the yield of 1,4-diphenylbutadiyne). (Reaction conditions: phenylacetylene (1.0 mmol); Cat. (5.7 mol% of the copper content); room temperature in air; reaction time (10 min)).

Tables

Components	$\frac{\underline{Si}_{out}}{\underline{Si}_{in}} \underbrace{\underline{C}_{out}}_{\underline{C}_{in}}$
Core-shell hybrid microspheres	0.499
Homogeneous hybrid microspheres	0.908

Table 1. Element ratios inside and outside the microspheres

No of cycles	Yield	Conversion
1	>96% (10 min)	>96%
2	>95% (10 min)	>95%
3	>95% (10 min)	>95%
4	>92% (10 min)	>92%
5	>90% (10 min)	>90%
6 (2 nd day)	>86% (30 min)	>86%
	>64% (10 min)	>64%
7 (3 rd day)	>86% (30 min)	>86%
	>61% (10 min)	>61%
8 (4 th day)	>85% (30 min)	>85%
	>56% (10 min)	>56%

 Table 2. Recycling of the catalyst

Table 3 XPS results	of the supported and	non-supported	catalysts
Table 5. At 5 lesuits	of the supported and	i non-supporteu	catarysis

Times of use	Cu _{2p} (supported)	Cu _{2p} (non-supported)
0	932.47	932.6
2	932.46	932.43
6	932.32	932.32



Figure 1







Figure 3



Figure 4



Figure 5



Figure 6



supported catalyst weight / mg

Figure 7



Figure 8