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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Double-shelled hollow mesoporous silica nanosphere as acid-base bifunctional catalyst for cascade reactions

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Double-shelled hollow mesoporous silica nanosphere (HMS-Al@MS-NH₂) has been successfully obtained using shell-byshell strategy, by which the isolated acidic (-Al) and basic (-NH₂) sites were spatially incorporated in different shells. The characterization results indicate that HMS-Al@MS-NH₂ possesses hollow void and mesopores in both shells, which favor the mass transfer of the reactants and products. As a spatially isolated acid-base bifunctional catalyst, HMS-Al@MS-NH₂ proved to exhibit high catalytic performances in one-pot deacetalization-Knoevenagel cascade reaction. Under the optimized conditions, the conversion of benzaldehyde dimethyl acetal approached *ca*.100% for 2 h at 110 °C, mainly attributed to the isolated acidic and basic sites and to the hollow architecture and mesopores in the shells. Notably, the catalyst could be reused up to 4 times without obvious loss of activity and selectivity, pointing to the high stability of the active acidic and basic sites in the framework. Moreover, the double-shelled hollow mesoporous silica spheres are also active and selective for the other cascade sequence of deacetalization-Henry reaction.

Introduction

Cascade reaction is a one-pot procedure that allows at least two reactions to proceed consecutively without any isolation of intermediates. This process can not only shorten the synthetic route but also decrease the content of gratuitous waste with high atom economy.^{1, 2} Therefore, the subject of cascade reaction has received considerable attention and elicited wide spread interest in the field of chemical synthesis.³⁻⁵ For efficiently catalyzing a cascade reaction, the key is designing suitably multifunctional catalysts (in particular, the heterogeneous catalyst) that should contain at least two types of active sites. High yield of the target products synthesized by multiple synthesis steps can be prepared in one pot under a suitable multifunctional catalyst.⁶⁻¹⁸ Some multifunctional groups have been successfully incorporated into heterogeneous catalysts through direct co-condensation and/or post grafting procedure. However, the acid-base bifunctional catalyst is less reported because of mutual destruction of active sites in the one-pot synthetic process. In order to overcome the neutralization effect of incompatible groups, a good idea is that the antagonist functions should be spatially isolated to coexist on one catalyst.¹⁹ There are several ways to achieve these.²⁰⁻³³ As yolk-shell formation is successfully fabricated,³⁴ the issue of the acid-base mutual neutralization is

nicely addressed to some extent.³⁵⁻⁴³ Moreover, either the core or the shell precisely contains the different active sites. For instance, Yang et al.²⁸ reported a base core (-NH₂) and an acidic shell (-SO₃H) were located in yolk-shell nanoreactor by organosilane-assisted selective etching method, which showed high catalytic activity in a one-pot deacetalization-Henry cascade reaction. Also, Song et al.⁶ reported another volk-shell nanosphere with the acid sites and the basic groups in the inner core and the outer shell, respectively, which led to further activity and selectivity due to the reasonable spatial order of acid-base sites for cascade reaction sequences. However, up to now, the acid sites in the acid-base bifunational catalyst are mostly provided by acidic organic compounds in the acid-base cascade reactions. One drawback of these materials is that the strength of acid is relatively weak with the certain alkalinity, i.e. the interaction of acid-base pairs is not perfectly matched, on one catalyst.^{44, 45} Therefore, it is always a challenge that how to tune the interaction and ensure the spatial isolation of acid-base pairs for developing a highly active catalyst in the acid-base cascade reactions.

The diffusion blockage and direction of mass transportation in catalysts is another important factor to effect the catalytic performances of a heterogeneous catalyst. The hollow void within the mesoporous materials could dramatically shorted the pore channels, thus the diffusion blockage become less significant and the active sites in the inner surface of the mesoporous can be utilized more effectively.^{35, 46-49} Meanwhile, multiple shelled mesoporous materials make it easier that the different active sites can be located in the catalyst and the reactants can be dispersed evenly and fast to each other.

Herein, a double-shelled hollow mesoporous silica nanosphere $(HMS-AI@MS-NH_2)$ as acid-base bifunctional catalyst with an acidic

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Electronic Supplementary Information (ESI) available: Fig. S1-S5.

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inner shell (-Al) and a basic outer shell (-NH₂) was fabricated. By using the sol-gel chemistry, thus, the shells formed step-by-step, the different active sites can be spatially isolated and the functionalization of different shells of the catalyst can be accurately controlled. The combination of hollow architecture and mesoporous structure successfully offered a shortened diffusion pathway for the reactants and products. The catalytic efficiency of the doubleshelled hollow mesoporous nanosphere for catalyzing deacetalization-Knoevenagel and deacetalization-Henry cascade reactions was demonstrated.

Experimental Section

Materials

No further purification of chemicals before experiments.

Preparation of polystyrene (PS) template

Based on the emulsion polymerization method, the synthetic procedure of polystyrene template was illustrated as follows. Under N₂ atmosphere, 1.5 g of polyvinyl pyrrolidone (PVP) was dissolved in 72 mL of deionized water in a three-necked flask. Then, 8 g of styrene (extracted by 10% NaOH solution for three times) was added slowly to the above solution, and the mixture was stirred at the speed of 170 rpm to obtain a uniformly distributed solution. For polymerization, 8 mL of deionized water with 0.26 g of 2,2azobisisobutyronitrile (AIBN) was added into the mixture, and then the reaction was proceeded for 24 h in oil bath at 70 °C. After being kept statically, the suspension was centrifuged, and the white polystyrene was washed with deionized water for twice and dried in oven at 60 °C. Then, the polystyrene microspheres were dispersed in 15 mL of deionized water with ultrasonic to get a uniformly distributed suspension. Finally, PS template was obtained.

Preparation of single-shelled HMS-AI

In a typical run, 18 mL of deionized water and 50 mL of ethanol with 2 g of cetyltrimethyl ammonium bromide (CTAB), 2 mL of polystyrene suspension, and 8.5 mL of NH₃·H₂O were stirred together at room temperature for 15 min. Then, 0.0731 g of aluminum isopropoxide solution (AIP, dissolved in 4 mL ethanol) was added and 2 mL of tetraethyl orthosilicate (TEOS) was slowly added into above solution. The mixture was reacted for 24 h. then the solution was centrifuged, washed and dried at 60 °C. After all, PS@Al-SiO₂ was calcined for 8 h at 550 °C to obtain a single-shelled hollow mesoporous silica nanosphere containing aluminium (HMS-AI).

According to the above-mentioned preparation procedure, a single-shelled HMS-Al with tunable molar ratios of silicon to aluminium at 100: 1, 25: 1 and 10: 1 can be obtained by altering the using amount of AIP. For a comparison, hollow mesoporous silica nanosphere without containing aluminium has been prepared via the similar method.

Preparation of double-shelled HMS-Al@MS-NH₂

The preparation route of double-shelled hollow mesoporous silica nanosphere (HMS-Al@MS-NH₂) was on the basis of single-shelled HMS-AI. 2 g CTAB was dissolved into a mixed solution with 18 mL of



Scheme 1 Scheme for the preparation of double-shelled mesoporous HMS-Al@MS-NH₂.

deionized water and 50 mL of ethanol, then 4 mL deionized water with 0.063g HMS-Al (ultrasonic treatment) and 8.5 mL NH₂·H₂O were added into the mixture at room temperature. Then, 100 μL of TEOS and 21 µL of aminopropyltriethoxysilane (APTES) were added to react for 24 h. The mixture was centrifuged, washed with deionized water and ethanol solution, dried in oven at 60 °C. To remove the surfactant CTAB, the obtained samples were refluxed with 4 mL of concentrated HCl aqueous solution and 60 mL of ethanol solution at 80 °C for 24 h. Finally, a double-shelled HMS-Al@MS-NH₂ catalyst was obtained (Scheme 1).

The final product was designated as HMS-AI@MS-NH₂-x, where x refers to the molar ratio of Si to Al in the original mixture. For a control experiment, mono-functional catalyst with comparable concentration of amino groups and the same double-shelled structure (HMS@MS-NH₂) was prepared by similar methods.

Catalytic tests

The deacetalization-Knoevenagel reaction of all substrates was carried out in a glass flask under magnetic stirring. In a typical run, 3 mL of methylbenzene and 40 mg of HMS-Al@MS-NH₂ were stirred in the flask for 5 min. Then, 0.5 mmol of benzaldehyde dimethyl acetal, 1 mmol of ethyl cyanoacetate, 0.1 mL of ethylbenzene and 0.05 mL of deionized water were added and the reaction proceeded at 110 °C for a certain time. The yield of benzyl cyanide ethyl acetate (target product) was evaluated as the activity of reaction. Using a gas chromatograph (GC Agilent-7890A) equipped with an FID analysed reaction products. Ethylbenzene was used as the internal standard.

Characterizations

X-ray diffraction (XRD) was measured on a Bruker D8 Advance instrument using Cu K α radiation (wavelength λ = 0.15418) in the range of 5-8° (2 θ) at a rate of 0.01°/min. Content of nitrogen was measured by elemental analysis on an Elementar Vario MICRO cube system. The isotherms of nitrogen adsorption-desorption was obtained by a Micromeritics ASAP 2020 system at liquid nitrogen temperature. The samples were outgassed under 200 °C for 240 min with a heating rate of 10 °C/min before measurements. Molar ratios of Si/Al were measured by elemental analysis on an Agilent ICP-MS 7500c inductively coupled plasma mass spectrometer. Scanning electron microscopy (SEM) images were taken on a Hitachi S-4300 apparatus running at 0.5~30 kV. Transmission electron

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microscopy (TEM) images were carried out on Hitachi H-7650 electron microscope running at 200 kV. Nuclear magnetic resonance (²⁹Si solid-state NMR) was conducted by Bruker AVANCE III spectrometer operating to judge the coordination environment of atoms and to analyse the content of elements. Gas chromatograph (GC Agilent-7890A) equipped analysed reaction products. X-ray photoelectron spectra (XPS) was used to characterize the chemical state of elements in the as-prepared samples with PHI 5700 ESCA system equipped with an A1 $\mbox{K}\alpha$ radiation as a source (hu = 1486.6 eV). CO_2 -TPD was measured with ChemBET Pulsar TPD equipment (Quantachrome, USA) to analyse the uptake of CO₂. The typical process as follows: 100 mg of HMS-Al@MS-NH₂-25 sample was pretreated at 100 °C for 20 min under 30 mL/min helium flow. After the temperature was decreased to 75 °C under helium flow, CO₂ sorption was started under 10 mL/min CO_2 flow for 30 min. Then the temperature was reduced to 30 $^{\circ}C$. Finally, the desorption test was performed under 50 mL/min helium flow through the temperature at a rate of 5 °C/min from 30 to 150 °C and kept 150 °C for 30min. By calculating the amount of desorbed CO₂ from the calibrated desorption curve, then the capacity of CO₂ uptake or sorption in millimole of CO₂ per gram of sorbent (mmol/g-S) was obtained. ²⁷AL MAS NMR spectrum was analysed by Bruker-DRX-400 spectrometer.

Results and Discussion

Characteristics of the catalysts

SEM and TEM images were applied to determine the morphology and structure of the synthesized samples. Clearly, the HMS-AI spheres possessed uniform size (Fig. 1a, Fig. S1A and S1C) at ca. 495-500 nm, which was regardless of ratios of Si/AI. It could be seen from the broken sample that it was indeed a hollow structure when the polystyrene template was removed. When the second layer was covered, the samples still possessed the spherical structure (Fig. 1b, Fig. S1B and S1D). Compared with the single-shelled ones, the diameters of the double-shell samples were increased by ca. 30 nm, which indicated that they were composed of double shells. According to the view of the broken sample, the double-shelled mesoporous spheres retained the hollow structure, showing that the condensation of TEOS and APTES only occurred on the outer shell of the HMS-Al sphere.

TEM images (Fig. 1c) indicated that the polystyrene template was completely removed after calcination at high temperature. The double-shelled structure was confirmed by comparing the shell thickness of HMS-AI-25 and HMS-AI@MS-NH₂-25, giving at 96 and 118 nm, respectively. Such increase for the shell thickness should be



DOI: 10.1039/C7NJ04670G

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Fig. 1 SEM images of (a) HMS-AI-25 and (b) HMS-AI@MS-NH2-25 and TEM images of (c) HMS-AI-25 and (d), (e), (f) HMS-AI@MS-NH₂-25.

strongly related with the covered second shell formed after the condensation of TEOS and APTES. Notably, it was apparent from the high magnification TEM image (Fig. 1e) that HMS-Al@MS-NH₂-25 was composed with two different shell layers (the red circle is the boundary between two shells). In addition, both shells of HMS-Al@MS-NH₂-25 contained abundant worm-like mesopores, which was in good agreement with the XRD results (Fig. S2). Based on the preparation scheme, it was reasonable to consider that the acid Al sites and basic amino sites were isolated and located in different shells.

To get a more defined mesoporous architecture, a series of HMS-Al@MS-NH₂-x with various ratios of silicon to aluminium were recorded by the nitrogen adsorption/ desorption measurement. All the samples were typical type-IV isotherms (Fig. 2A),⁵⁰ pointing to the presence of mesoporous template from CTAB micelles. Based on the pore size distribution curves,

Table 1 Texture properties of HMS-AI@MS-NH2-x							
catalyst	S _{BET} (m²/g)	Pore vol. (cm ³ /g)	Pore size (nm)	N content (mmol/g)	Si/Al (molar ratio)		
HMS-AI@MS-NH ₂ -10	1100	0.46	2.1	0.82	39		
HMS-Al@MS-NH ₂ -25	1302	0.60	2.4	0.62	82		
HMS-Al@MS-NH ₂ -100	1350	0.61	2.4	0.67	477		



Fig. 2 (A) Nitrogen adsorption-desorption isotherm and (B) BJH pore size distribution curves of (a) HMS-Al@MS-NH₂-10, (b) HMS-Al@MS-NH₂-25 and (c) HMS-Al@MS-NH₂-100. For sake of clarity, spectra b and c are offset along the vertical axis by 50 and 150 cm³/g, respectively.

the mesopores were centered at 2.4 nm (Fig. 2B). It was clear that the molar ratio of Si/Al had no influence on the mesopore size. The other texture properties were listed in Table 1.

²⁹Si solid-state NMR spectrum of HMS-Al@MS-NH₂-25 was performed to confirm that the ammonia propyl organosilane was condensed into the hollow mesoporous framework (**Fig. 3**). In addition to Q² [Si(OR')₂(OSi)₂, -92 ppm], Q³ [Si(OR')(OSi)₃, -100 ppm] and Q⁴ [Si(OSi)₄, -110 ppm] signals, two types of silicon species (-56 ppm and -67 ppm) were observed, which corresponded to T² [RSi(OSi)₂OH] (R represents-(CH₂)₃-NH₃) and T³ [RSi(OSi)₃], respectively.²⁸ The presence of T² and T³ signals confirmed that the organic groups and the silica surface formed the strong covalent linkage. Meanwhile, XPS also confirmed the presence of amino groups (402.7 eV) in the catalyst (**Fig. S3**).^{51, 52} The CO₂ uptake was measured at 81.78 mmol/g by the sorption (Fig. S5).^{53, 54}

²⁷Al MAS NMR spectroscopy was applied for determining the coordination of the acidic Al sites in the double-shelled mesoporous silicas. The peak of 55 ppm and 0 ppm corresponded to tetrahedral (AlO₄) and octahedral (AlO₆) coordination, respectively (**Fig. S4**).⁵⁵ Such NMR result indicated that the Al sites in HMS-Al@MS-NH₂-25 were mainly tetrahedral.

DOI: 10.1039/C7NJ04670G

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Deacetalization-Knoevenagel reaction

With the co-existence of acid-base bifunctional active species, all of the three materials were applied as catalyst in deacetalization-Knoevenagel cascade reaction (Table 2). It was obvious that only trace conversion could be monitored in blank and with pure SiO₂ sphere. When the materials containing Al sites and amino groups in the shells were applied as efficient catalysts, both of the conversion and selectivity could be as high as ca. 100%. Besides, it could be seen that only intermediate (B) was generated over HMS-Al and trace yield of the product (C) was achieved. One can conclude that the first step (deacetalization reaction) was mainly catalyzed by the acid Al species and the second step (Knoevenagel reaction) by amino groups. (entries 3, 5 and 6). It was worth nothing that the conversion of A was 50.8% when the reaction was carried out in absolute toluene, but it could be increased to almost 100% by adding trace water in the reaction solution. This indicated that the existence of water could accelerate the deacetalization process (as displayed in entries 3 and 4) and had no influence on the Knoevenagel reaction. Based on the observation that the materials with molar ratio of Si/Al ranging from 10 to 100 all gave almost 100% conversion and selectivity when the reaction time was set as long as 2 h, it was reasonable to believe that Al sites were highly active for the deacetalization. For better understanding the advantages of the structural design of HMS-Al@MS-NH₂ sample, the catalytic performance of the physical mixture composed of HMS-AI and HMS@MS-NH₂ had also been checked. The activity on the physical mixture of HMS-Al and HMS@MS-NH₂ was relatively lower than HMS-Al@MS-NH₂-25 (entries 9 and 11), which confirmed the advantages of the structural design of HMS-Al@MS-NH₂ sample.

For all the catalysts tested, the catalytic activity increased gradually along with time, and HMS-Al@MS-NH₂-25 arrived a plateau emerged after 60 min. Note here that the yield of the final product reached 100% during the reaction process. At the beginning of the reaction time, a big difference in activity of HMS-Al@MS-NH₂-25, HMS-Al@MS-NH₂-100 and HMS-Al@MS-NH₂-10 was observed (**Fig. 4A**). HMS-Al@MS-NH₂-25 showed the higher reaction rate than HMS-Al@MS-NH₂-100 and HMS-Al@MS-Al@MS-NH₂-10.



Fig. 3 ²⁹Si solid-state NMR spectrum of HMS-Al@MS-NH₂-25 (T² : -56 ppm; T³ : -67 ppm; Q² : -92 ppm; Q³ : -100 ppm; Q⁴ : -110 ppm).

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 Table 2 Deacetalization-Knoevenagel cascade reaction sequence catalysed by different catalysts

		Me acid site H2O B	$-CHO \xrightarrow{\text{basic site}}_{NC \land CO_2Et} \bigcirc C$	CO ₂ Et		
Entry	Catalyst	Conv. of A (%)	Yield of B (%)	Yield of C (%)	Sel. of C (%)	
1	No catalyst ^a	1.3	1.3	0	0	
2	Pure SiO ₂ ^a	2.7	2.7	0	0	
3	HMS-Al ^a	50.8	50.8	0	0	
4	HMS-AI ^b	~100	~100	0	0	
5	HMS@MS-NH ₂ ^a	12	0	12	~100	
6	HMS-Al@MS-NH ₂ -25 ^a	76	16.7	59.3	78	
7	HMS-AI@MS-NH ₂ -25 ^b	~100	41.6	58.4	58.4	
8	HMS-AI@MS-NH ₂ -10 ^c	97.6	0	97.6	~100	
9	HMS-AI@MS-NH ₂ -25 ^c	~100	0	~100	~100	
10	HMS-AI@MS-NH ₂ -100 ^c	~100	0	~100	~100	
11	HMS-Al and HMS@MS-NH ₂ ^c	~100	14.3	85.7	85.7	

^a Reaction conditions: benzaldehyde dimethyl acetal (0.5 mmol), ethyl cyanoacetate (1.0 mmol), toluene (3 mL), catalyst (40 mg), reaction temperature is 110 °C, reaction time is 20 min. Conversion and yield were determined by GC analysis using hexane as internal standard. ^b 50 μ L H₂O. ^c 50 μ L H₂O, Reaction time is 2 h.

By considering that octahedral Al sites in a porous silica possessed weaker acid strength than tetrahedral ones, the relatively lower conversion of the benzaldehyde dimethyl acetal over HMS-Al@MS-NH₂-10 was possibly attributed to the different coordination environment (octahedral) compared with that (tetrahedra) in HMS-Al@MS-NH₂-25 and HMS-Al@MS-NH₂-100.

Leaching test was performed to evaluate if the active acidic and basic species leached in the reaction mixture during the catalysis procedure. HMS-Al@MS-NH₂-25 was separated from the reaction mixture at 110 °C after 20 min. The filtrate was divided into two sections: one was further heated for 100 min at 110 °C and the other was analyzed by GC. Notably, no further reaction was observed after the catalyst had been removed, indicating that no

active acidic and basic sites leached from HMS-Al@MS-NH $_2$ -25 during the reaction process under the given reaction conditions (Fig. 4B).

CN

A catalyst is necessarily evaluated by recyclability which is an important parameter. The catalyst was recycled via calcination under N₂ for 2 h at 200 $^{\circ}$ C after each run and the active sites could be regenerated. It was clear that catalytic activity was no significant loss when reusing HMS-Al@MS-NH₂-25 in four successive catalytic runs, indicating the high stability of the active sites. This is in good agreement with the result from leaching test (**Fig. 5**).

The assets of HMS-Al@MS-NH₂-x are constituted by its mesoporosity and isolate acidic and basic sites located in different shells, which enable the cascade reaction. To show that this effect



Fig. 4 (A) Conversions of the deacetalization-Knoevenagel of benzaldehyde dimethyl acetal with (a) HMS-Al@MS-NH₂-25, (b) HMS-Al@MS-NH₂-100 and (c) HMS-Al@MS-NH₂-10 versus reaction time; (B) leaching test for HMS-Al@MS-NH₂-25 during the reaction: (a) yields of product with HMS-Al@MS-NH₂-25 and (b) yields of product after the catalyst of HMS-Al@MS-NH₂-25 was filtered from the reaction media after 20 min.

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	A OMe aci	d site I₂0 B	CHO basic site CH ₃ NO ₂	D	_N02	
Entry	Catalyst	Conv. of A (%)	Yield of B (%)	Yield of D (%)	Sel. of D (%)	
1	HMS-Al@MS-NH ₂ -10 ^ª	98	0.3	97.7	99.6	This work
2	HMS-AI@MS-NH ₂ -25 ^a	~100	0	~100	~100	This work
3	HMS-AI@MS-NH ₂ -100 ^a	79.6	0.5	79.1	99.4	This work
4	YS-NH ₂ @SOH ₃ ^b	100	trace	>99	—	Ref. ²⁸

^a Reaction conditions: benzaldehyde dimethyl acetal (0.5 mmol), nitromethane (5 mL), catalyst (40 mg), reaction temperature is 90 °C, reaction time is 14 h.

^b Reaction conditions: benzaldehyde dimethyl acetal (0.5 mmol), nitromethane (5 mL), catalyst (100 mg), reaction temperature is 90 °C, reaction time is 22 h.



Fig. 5 Catalytic activity with repeated use of HMS-Al@MS-NH₂-25 in the deacetalization-Knoevenagel of benzaldehyde dimethyl acetal via calcination approach.

was not limited to the deacetalization-Knoevenagel reaction, HMS-Al@MS-NH₂-x was tested for the other cascade reaction, i.e. onepot deacetalization-Henry reaction and HMS-Al@MS-NH₂-x proved to exhibit good performances (**Table 3**). The conversion and selectivity of the double-shelled catalysts of HMS-Al@MS-NH₂-10 and HMS-Al@MS-NH₂-25 in the deacetalization-Henry cascade reaction were very promising when compared with the catalytic performance obtained with other acid-base bifunctional yolk-shell nanoreactor of YS-NH₂@SOH₃, even though more catalyst was used and longer reaction time was set in the case of YS-NH₂@SOH₃ (see reaction conditions in **Table 3**).²⁸

As shown in **Fig. 6**, the reactants (benzaldehyde dimethyl acetal) could pass through the hollow space to reach the inner shell during the catalytic process, where they were converted into the intermediate species (benzaldehyde) via the reaction of deacetalization. In the outer shell, the intermediate (B) diffused from the inner shell could be further catalyzed to the target product (ethyl benzyl cyanoacetate).⁶



Fig. 6 Schematic reaction flow of the two-step cascade reaction sequences on the double–shelled structured bifunctional catalyst HMS-Al@MS-NH₂.

In summary, double-shelled hollow mesoporous silicas have been designed via a two-step condensation approach, by which acidic frame worked AI species were incorporated in the inner shell and amino groups were tethered on the outer shell. The double-shelled construction realized spatial separation of acidic and basic sites and the mesopores in the shells favored the mass transfer in and out of the hollow interior. Such double-shelled hollow materials proved to be highly active and selective for the deacetalization-Knoevenagel cascade reaction, giving ca. 100% conversion of benzaldehyde dimethyl acetal and ca. 100% selectivity towards the target product of ethyl benzyl cyanoacetate. Importantly, HMS-Al@MS-NH2-25 was a stable catalyst without leaching of active sites and could be successfully reused in catalytic cycles without obvious loss of activity. Moreover, the double-shelled hollow materials with mesopores were also active and selective for the deacetalization-Henry cascade reaction.

Conflicts of interest

There are no conflicts to declare.

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Conclusions

Published on 26 January 2018. Downloaded by Fudan University on 30/01/2018 04:17:12.

Acknowledgements

We thank the financial support from National Natural Science Foundation of China (51472062) and the Opening Project of Key Laboratory of Polyoxometalate Science of Ministry of Education.

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Graphical abstract



Table of content

Double-shelled hollow mesoporous silica nanosphere as acid-base bifunctional catalyst for cascade reactions.