

Article

Compartmentalization of Incompatible Catalysts Within Supraparticles for Continuous-Flow Cascade Catalysis

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Abstract

Supraparticles (SPs) with millimeter-scale structural features have emerged as promising functional materials for industrial catalytic applications, owing to their unique capability to integrate multiple catalytic components and adapt to continuous-flow reaction systems. However, the rational design and targeted fabrication of high-performance SPs for incompatible tandem catalysis remain underexplored. Herein, we developed a liquid-marble droplet-template strategy for fabricating SPs that spatially integrate incompatible catalytic sites for cascade reactions. Notably, the obtained SPs possess high mechanical strength and thus allows for packing into fixed-bed reactors for continuous-flow catalysis. As exemplified by the acidic-amine-catalysis deacetalization–Henry reaction, our systems exhibit high conversion (>99%), yield (75%), and long-term operational stability (200 h). This work presents a feasible strategy for the controllable construction of high-efficiency bifunctional supraparticle catalysts, which may offer some insights into the design and potential industrial application of incompatible acid-base cascade catalytic systems.

Keywords: supraparticles; incompatible; cascade reactions; continuous flow

1. Introduction

One-pot multistep tandem catalysis represents a pivotal route for achieving green and highly efficient synthesis, because of its distinctive advantages, including eliminating intermediate separation, overcoming thermodynamic equilibrium constraints, enhancing reaction efficiency, and reducing energy consumption [1–5]. To realize the concept, researchers have spatially compartmentalized incompatible catalytic sites in different beads (either micro-, nano-, or millimeter-scale) [6–14]. However, existing methods are still facing difficulties in precisely controlling tandem reactions at nanoscale levels while simultaneously maintaining the catalyst size at the millimeter scale [15–20]. We envisage that an ideal catalyst suitable for filling into fixed-bed reactors should be: (i) millimeter in size, to enable the balancing of pressure drop, mass transfer, heat transfer, and mechanical strength; (ii) able to compartmentalize incompatible catalysts in micro- or nanoscale, while still ensuring their close proximity; (iii) have multiple catalytic active sites working synergistically; and (iv) exhibit excellent long-term operational stability.



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Supraparticles (SPs)—macroscopic aggregates self-assembled from nano- or microscale building blocks—have recently emerged as promising materials due to their attractive structural tunability and modifiable catalytic activity [21–28]. A typical strategy for the fabrication of SPs relies on self-assembly driven by weak noncovalent interactions [29–32]. However, this strategy requires precise control over the balance of interparticle interactions and nucleation-growth dynamics, making it difficult to fabricate uniform spherical SPs with complex multicomponent architectures. An alternative strategy employs droplet-template-based assembly, such as emulsion templating [33,34], microfluidic assembly [35–38], and spray drying [39–42]. However, these strategies suffer from different problems. For instance, conventional emulsions suffer from poor stability and thus cannot readily yield millimeter-scale SPs; microfluidic platforms also encounter technical barriers to macroscopic SP fabrication. Spray drying relies on rapid high-temperature solvent evaporation, which readily induces droplet deformation and structural cracking, precluding the formation of regular millimeter spheres. Accordingly, the development of new strategies for the fabrication of millimeter SPs is of paramount importance.

In pursuit of this goal, considerable efforts have been devoted to constructing SPs using liquid-marble droplet-template strategies [27,43–46]. For example, Wang et al. reported a hydrogel-stabilization strategy for SPs: co-assembly of SiO₂ nanoparticles and sodium alginate followed by Ca²⁺ crosslinking raised the fracture force of resultant SPs to 6.04 N, furnishing mechanically stable supports for enzymatic cascade catalysis [43]. Yetkin et al. systematically characterized evaporative assembly of ellipsoidal colloids on superamphiphobic surfaces and proved that surfactant modulation effectively suppresses surface wrinkling to yield morphologically regular SPs [46]. Although these results are highly encouraging, studies on the practical compartmentalization of incompatible catalysts remain scarce, particularly those involving acid-base catalyst pairs.

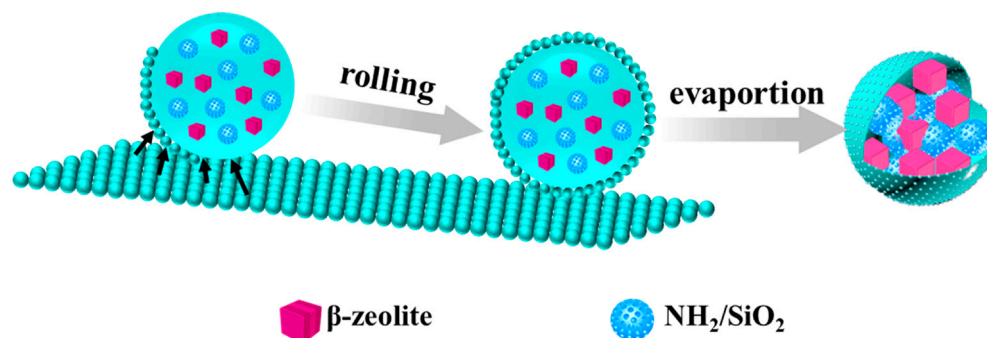
Inspired by the spatial organization of living cells, we introduced a simple co-assembly strategy for fabricating SPs that spatially integrate incompatible catalytic sites for cascade reactions. The unique architecture allows for spatial proximity of incompatible active centers while simultaneously ensuring their site isolation. Moreover, the number of sub-compartments and relative ratio of different sub-compartments can be precisely controlled. The obtained millimeter-sized SPs are then packed in a continuous-flow reactor for tandem catalysis, exhibiting high conversion (>99%), product yield (>75%), and long-term operation stability (200 h). This work offers a promising platform for designing efficient and durable tandem catalysts.

2. Results and Discussion

2.1. Design and Characterization of β -Zeolite-NH₂/SP Catalyst

To assess the capacity of millimeter-sized SPs for compartmentalization of incompatible catalysts, we chose a representative acid–base bifunctional composite system, in which β -zeolite and amino-modified silica nanospheres were used as acidic and amino sub-compartments, respectively. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed amino-grafted silica nanospheres with an average size of approximately 100 ± 10 nm (Figure S1a,b). Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA) further verified successful amine grafting on silica nanospheres (Figure S2a,b). Moreover, SEM and TEM observations confirmed that the β -zeolite exhibits the morphology of regular cuboid single crystals with a size of 25–100 nm (Figure S1c,d).

The fabrication of millimeter-sized SPs involved two steps (Scheme 1). An aqueous suspension containing 5 wt% β -zeolite and 15 wt% amino-modified SiO_2 (wt% relative to the total mass of water, β -zeolite, and amino-modified SiO_2 unless otherwise stated) was dropped onto a filter paper coated with hydrophobic silica powder, followed by rolling on this filter paper. Due to the adsorption at the solid-liquid interface, the hydrophobic silica powders were picked up from the filter paper, forming a protective hydrophobic shell around the water drops. The generated liquid marbles were transferred onto culture dishes. Then, evaporation of water from the liquid marbles under ambient conditions drove the assembly of an interior sub-compartment. The preparation process is straightforward, eliminating the need for other additives.



Scheme 1. Preparation of β -zeolite- NH_2 /SP catalyst.

The obtained millimeter-sized SPs showed uniform and discrete spherical morphology with an average diameter of 1.5 mm (Figure 1a). SEM images of a single millimeter-sized SP further confirm the well-defined spherical architecture (Figure 1b,c). SEM images of a cross-section of a single millimeter-sized SP demonstrate that β -zeolite and NH_2 -modified SiO_2 nanoparticles are densely distributed and intimately contacted within the spherical matrix (Figure 1d). High-resolution TEM shows that the silica and β -zeolite are uniformly distributed within the SPs (Figure 1e). EDX elemental mappings indicate that the Al from β -zeolite and the Si from NH_2 -modified SiO_2 nanoparticles are co-located within the millimeter-sized SPs (Figure 1f), which is consistent with the results from the cross-section SEM images. In addition, the inner structure of the SPs was also characterized through confocal laser scanning microscopy (CLSM). Specifically, β -zeolite and amino-modified silica nanospheres were separately labeled with FITC-I and Rhodamine B during the preparation of the SP-based catalyst. The results show that both red and green signals are distributed throughout the SPs (Figure S3), demonstrating that two types of particles were confined to the inner compartment of the SPs. These structural features are beneficial to the efficient progress of cascade catalytic reactions. In addition, the fabricated spherical composites achieved a high mechanical strength of 3.1 N, which is closely related to the unique interfacial interactions between different components. Specifically, the positively charged H^+ and Al^{3+} sites on β -zeolite can effectively interact with the amine groups of NH_2/SiO_2 , thereby reinforcing the overall structural stability. Moreover, β -zeolite- NH_2 /SPs exhibit good permeability to external molecules. Within only 60 s, fluorescence appears at the SP periphery, and after 240 s, the concave-shaped fluorescent pattern gradually changes to a bulge-shaped pattern, implying that fluorescent molecules reached the center of the SP. The fluorescent results indicate that our SPs have good permeability, even towards the fluorescent probe with relatively large molecular size (Figure S3). Such permeability is sufficient for catalytic reactions occurring inside the SP-based catalyst.

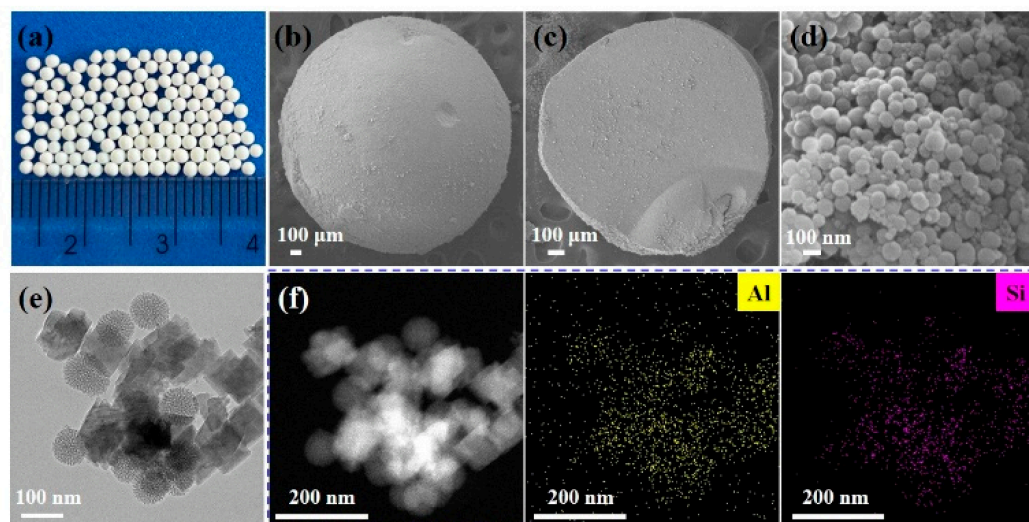


Figure 1. Characterization of the β -zeolite- NH_2 /SP cascade catalyst. (a) Appearance of the cascade catalyst. (b) SEM image showing the cascade catalyst. (c) SEM image showing the interior structure of the cascade catalyst, after being cut deliberately. (d) Magnified SEM image showing the interior structure of the cascade catalyst. (e) High-resolution TEM image showing the secondary structural units within the cascade catalyst. (f) Elemental mapping of the interior of the cascade catalyst.

2.2. Catalysis Performance of β -Zeolite- NH_2 /SiO₂ SPs

Integration of incompatible catalytically active sites into a single system is highly desirable for catalytic applications because it enables one-pot cascade catalysis with enhanced overall reaction efficiency [9,11,19,20,47–51]. Nevertheless, precise coordination of catalytic kinetics between different active sites at the nanoscale remains a major challenge, particularly for cascade reactions involving incompatible catalytic centers. To demonstrate the feasibility of our strategy, we selected the deacetalization–Henry cascade reaction as a model reaction. As a fundamental acid-catalyzed transformation in organic synthesis, deacetalization generates carbonyl intermediates that can undergo subsequent base-catalyzed reactions: specifically, the β -zeolite-catalyzed deacetalization of benzaldehyde dimethyl acetal to produce benzaldehyde, followed by the NH_2 /SiO₂-catalyzed Henry reaction of the in situ generated benzaldehyde (as illustrated in Figure 2a). In the reaction, 1,3-dinitro-2-phenylpropane was formed as a byproduct via Michael addition of β -nitrostyrene.

To evaluate the catalytic performance of the β -zeolite- NH_2 /SiO₂ SPs (β -zeolite and NH_2 /SiO₂ nanoparticles were co-assembled into millimeter-sized SPs), we first compared β -zeolite- NH_2 /SiO₂ SPs with their analogs in batch reactions at 70 °C. Batch reactions were chosen for the subsequent studies because they provide a simpler experimental platform and allow more rapid and straightforward evaluation of catalyst performance than continuous-flow systems while allowing direct comparison of nanoparticle-based catalyst configurations. Three catalyst configurations were evaluated: (i) a physical mixture of independent NH_2 /SiO₂ SPs (only NH_2 /SiO₂ nanoparticles were assembled into millimeter-sized SPs) and β -zeolite SPs (only β -zeolite nanoparticles were assembled into millimeter-sized SPs); (ii) a physical mixture of pristine NH_2 /SiO₂ and β -zeolite nanoparticles; and (iii) β -zeolite- NH_2 /SiO₂ SPs. The structural schematics of the three catalyst configurations (i–iii) are presented in Figure 2b. Under identical reaction conditions, for catalyst configuration (i), a 99% conversion of benzaldehyde dimethyl acetal and 84% yield of β -nitrostyrene were obtained after 24 h of reaction. For catalyst configuration (ii), the yield of β -nitrostyrene was 89%, slightly higher than that for catalyst configuration (i), although the conversions of benzaldehyde dimethyl acetal observed in these two cases were at the same level. Interestingly, using the catalyst configuration (iii), the yield of β -

nitrostyrene was 97%, and the conversion of benzaldehyde dimethyl acetal was maintained at 99%. Among the three catalyst configurations, the β -zeolite- NH_2/SiO_2 SPs exhibit a significantly higher yield than those obtained from the two control catalyst configurations. This enhancement is attributed to the nanoscale spatial proximity between the β -zeolite and NH_2/SiO_2 nanoparticles, which shortens the diffusion distance of the benzaldehyde intermediate and thereby facilitates its rapid transfer between the acid- and base-catalyzed steps. In all catalyst systems, the slightly lower product yield than substrate conversion is attributed to the minor formation of 1,3-dinitro-2-phenylpropane via the Michael addition of β -nitrostyrene.

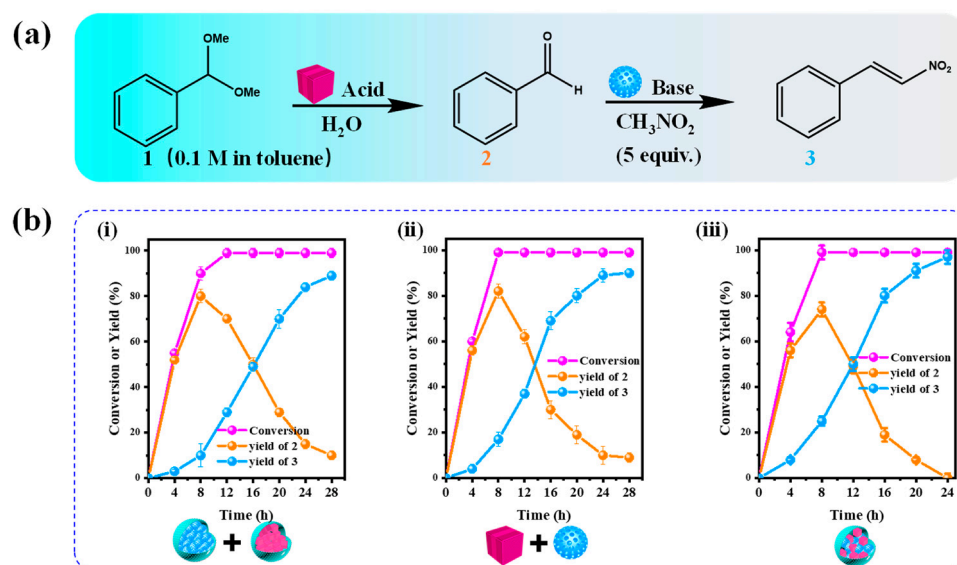


Figure 2. Results of the deacetalization–Henry cascade reaction over three analogous catalysts. **(a)** Reaction network of the cascade reaction. **(b)** Conversion and yield with time in batch systems. Reaction conditions: (i) Physical mixture of 30 mg NH_2/SiO_2 SPs (constructed by NH_2/SiO_2 nanoparticles as the secondary structural unit) and 10 mg β -zeolite SPs (constructed by β -zeolite nanoparticles as the secondary structural units); (ii) physical mixture of 30 mg NH_2/SiO_2 and 10 mg β -zeolite nanoparticles; (iii) 40 mg β -zeolite- NH_2 /SPs, prepared with 1:3 mass ratios of β -zeolite and NH_2/SiO_2 nanoparticles, 0.2 mmol benzaldehyde dimethyl acetal and 5 equiv. nitromethane, 2 mL toluene, 70 °C. Error bars represent standard deviation from three independent experiments.

To further demonstrate the importance of spatial compartmentalization of incompatible catalytic sites, NH_2 -functionalized β -zeolite (NH_2/β -zeolite), in which the acid and base sites are co-located on the same nanoparticles, was prepared as a control catalyst. As shown in Figure 3, using the NH_2/β -zeolite, only 25% conversion was obtained after 16 h of reaction. In contrast, the β -zeolite- NH_2/SiO_2 SPs achieved 99% conversion under identical reaction conditions.

To further improve the yield of β -nitrostyrene, the effect of the proportion of the two sub-compartment was investigated by increasing the NH_2/SiO_2 concentration while fixing the β -zeolite concentrations. The results showed that the conversion of benzaldehyde dimethyl acetal remained constant at 99% across different NH_2/SiO_2 ratios after 24 h of reaction. However, the yield of β -nitrostyrene gradually increased with increasing NH_2/SiO_2 ratio from 1:1 to 1:3, reaching a maximum value of 97% at a ratio of 1:3. Further increasing the NH_2/SiO_2 ratio to 1:4 did not lead to any additional improvement in yield (Figure 4). Additionally, the cycle stability of β -zeolite- NH_2 /SPs was also examined. Notably, the β -zeolite- NH_2 /SPs maintained 99% conversion and 93% yield after five cycles of reaction, indicating excellent catalytic stability (Figure S5).

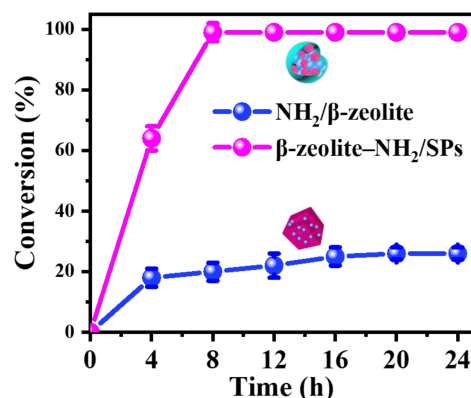


Figure 3. Conversions over time between β -zeolite- NH_2 /SPs and NH_2 / β -zeolite (amine grafted on β -zeolite). Other reaction conditions are the same as in Figure 2b. Error bars represent the standard deviation from three independent experiments.

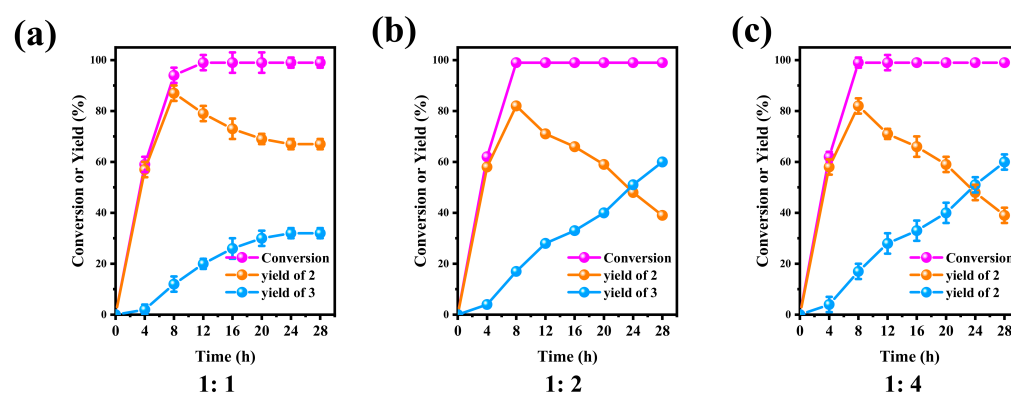


Figure 4. Conversion and yield over time in batch systems of SPs prepared with different mass ratios of β -zeolite to NH_2/SiO_2 . Keeping the amount of β -zeolite unchanged, the NH_2/SiO_2 was increased from (a) 10 mg, (b) 20 mg, to (c) 40 mg, respectively. Other reaction conditions are the same as in Figure 2b. Error bars indicate the standard error from 3 independent experiments.

Taken together, these excellent results underscore the advantages of our designed SP-based tandem catalysts, which feature acid and base sites positioned in distinct locations while remaining in close proximity.

2.3. Results of the Deacetalization–Henry Cascade Reaction over β -Zeolite- NH_2 /SPs in Continuous-Flow Systems

To further test the potential for practical applications of the β -zeolite- NH_2 /SPs catalysts, we packed β -zeolite- NH_2 /SPs in a fixed-bed reactor for continuous-flow catalysis. A solution of benzaldehyde dimethyl acetal and nitromethane was continuously pumped into the inlet of this reactor, and the product-containing stream was collected from its outlet (Figure 5a). As shown in Figure 5b, the conversion of benzaldehyde dimethyl acetal at steady state was 99%, the yield of β -nitrostyrene was 75–90% in spite of slight fluctuations, and almost none of the 1,3-dinitro-2-phenylpropane by-product was detected. After running for 200 h, the yield of β -nitrostyrene did not significantly decline, albeit at the expense of the flow rate. The above results can be ascribed to the shorter distance between acid and base catalytic species, which is favorable to timely transfer of the intermediate. Furthermore, the cascade catalyst worked very well in fixed-bed reactors for the other substrates, such as 1-(dimethoxymethyl)-4-methylbenzene; the conversion was maintained at the level of 99% over a period of 200 h, and the corresponding yield of β -nitrostyrene within 73–88% (Figure 5c). For less reactive substrates, such as 4-bromobenzaldehyde dimethyl acetal, a yield of 70–89% of β -nitrostyrene with >94% conversion was achieved

over 100 h (Figure S6). Notably, we found that the yield over β -zeolite-NH₂/SPs is much higher than that obtained in the two-stage arrangement (70–80%) (Figure S7). This can be ascribed to the shorter distance between different catalytic species, which is favorable to timely transfer of the intermediate.

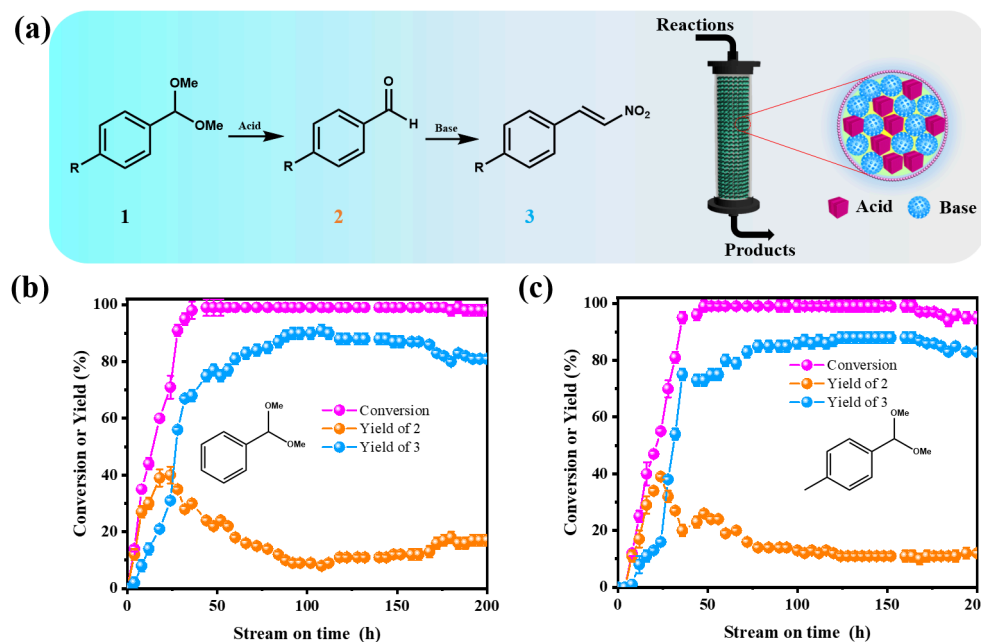


Figure 5. Results of the deacetalization–Henry cascade reaction over β -zeolite-NH₂/SPs in continuous-flow systems. Reaction conditions: 1.0 g β -zeolite-NH₂/SPs were packed in a fixed-bed reactor, 0.1 M substrate and 5 equiv. nitromethane in toluene, 70 °C. (a) Reaction network of the cascade reaction. (b) Continuous-flow cascade reaction using acetaldehyde dimethyl acetal as substrate, flow rate from initial 1.2 mL h^{−1} to 0.6 mL h^{−1} at the end. (c) Continuous-flow cascade reaction using 1-(dimethoxymethyl)-4-methylbenzene as substrate, flow rate from initial 1.0 mL h^{−1} to 0.6 mL h^{−1} at the end. Error bars indicate the standard error from 3 independent experiments.

To evaluate the structural stability of our catalysts, a series of characterizations was performed. Optical microscope imagery showed that the β -zeolite-NH₂/SiO₂ SPs retained their original spherical morphology without discernible surface cracks or fractures after long-term continuous-flow catalysis (Figure 6a). SEM image of the cross-section confirmed that the interior structure of β -zeolite-NH₂/SiO₂ SPs remained intact (Figure 6b). TEM image of the catalyst confirmed that the NH₂/SiO₂ and β -zeolite are uniformly distributed within the SPs (Figure 6c). The mechanical strength test revealed that the mechanical robustness of β -zeolite-NH₂/SiO₂ SPs was well preserved after the prolonged continuous reaction time (Figure 6d). Moreover, thermogravimetric analysis (TGA) further showed nearly identical weight-loss profiles before and after long-term continuous-flow catalysis (Figure 6e), confirming the excellent structural integrity and chemical stability of the catalyst. These comprehensive characterizations demonstrate the outstanding operational stability of the as-prepared SP catalyst, verifying its promising application potential in practical cascade catalysis. Benefiting from the high mechanical strength of SPs and their surface hydrophobic silica coating, an effective barrier is formed to inhibit the aggregation of discrete catalyst beads.

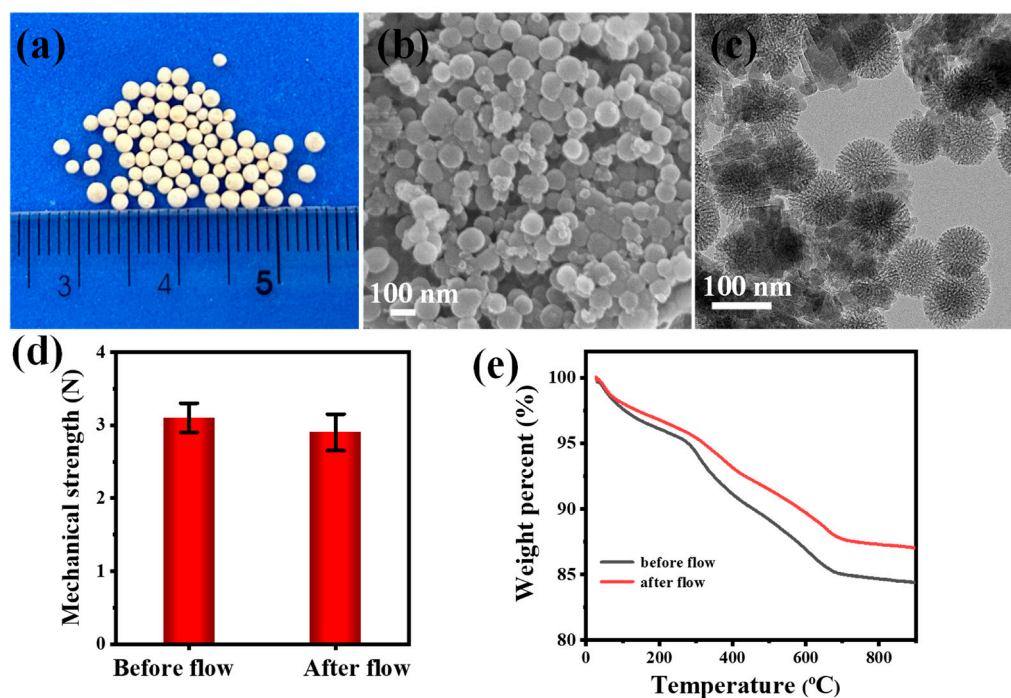


Figure 6. Characterization results of the β -zeolite- NH_2 /SPs after continuous-flow reaction. (a) Appearance of β -zeolite- NH_2 /SPs after 200 h of long-term continuous-flow catalysis. (b) SEM image showing the secondary structural units within the cascade catalyst after continuous flow. (c) TEM image showing the secondary structural units within the cascade catalyst after 200 h of continuous flow catalysis. (d) Mechanical strength of SPs before and after the continuous flow; error bars indicate the standard error from a 20-sample average. (e) TGA profiles of SPs before and after continuous flow.

3. Materials and Methods

3.1. Materials

n-dodecane (AR) and cyclohexane (AR) were procured from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane (90%), tetraethyl orthosilicate (TEOS, AR), *n*-hexylamine (99%), hexadecyltrimethylammonium chloride (CTAC, 97%), 3-aminopropyltriethoxysilane (APTES, 99%), triethanolamine (TEA, AR), 3-[2-(2-aminoethylamino)ethylamino]propyltriethoxysilane (90%), fluorescein isothiocyanate isomer I (FITC-I, CAS No. 3326-32-7) and Rhodamine B (CAS No. 81-88-9) were purchased from Aladdin (Shanghai, China). β -zeolite was purchased from Tianjin Nankai Catalyst Co., Ltd. (Tianjin, China). Toluene (AR), benzaldehyde dimethyl acetal, 1-(dimethoxymethyl)-4-methylbenzene, 4-bromobenzaldehyde dimethyl acetal, benzaldehyde, and nitromethane were purchased from Sinopharm Group (Shanghai, China). Commercially hydrophobic silica was Degussa fumed silica R972, purchased from Degussa (China) Investment Co., Ltd. (Beijing, China). Water used in this study was deionized water.

3.2. Catalyst Preparations

3.2.1. Preparation of β -Zeolite- NH_2 /SP Cascade Catalyst

β -zeolite and NH_2/SiO_2 nanoparticles with a prescribed mass ratio were dispersed in deionized water to form an aqueous suspension containing 20 wt% nanoparticles and 80 wt% water. After thorough homogenization, the suspension was loaded into a syringe with a 0.5 mm orifice. The suspension was then continuously dropped onto a bed composed of hydrophobic fumed silica (R974). Upon impact, the droplets rolled on the powder bed to form liquid marbles. The as-formed liquid marbles were subsequently transferred

onto filter paper. Water within the liquid marbles was slowly evaporated under ambient conditions (25 °C), yielding the desired millimeter-sized SPs.

3.2.2. Preparation of Other SP Cascade Catalysts

Other procedures are the same for the synthesis of SPs made of β -zeolite and NH_2/SiO_2 . The mass ratio of β -zeolite and NH_2/SiO_2 was changed.

3.3. Catalyst Characterization

Transmission electron microscopy (TEM) images were obtained on a JEM 2000EX (JEOL Ltd., Akishima, Japan). Samples for TEM observations were prepared by dispersing the sample powder in ethanol using ultrasound and then allowing a drop of the suspension to evaporate on a copper grid covered with a holey carbon film. EDS elemental maps were recorded on this instrument. Scanning electron microscope (SEM) images were obtained on a JEOL JSM-6700F field-emission electron microscope (JEOL Ltd., Akishima, Japan). Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer (Thermo Electron Corporation, Madison, WI, USA) over the range 4000–400 cm^{-1} with 64 scans and a resolution of 2 cm^{-1} . Thermogravimetric (TG) measurement was performed on TA Q-600 instrument (TA Instruments, New Castle, DE, USA). Gas chromatography (GC) analysis was carried out on an Agilent 7890 analyzer (Agilent Technologies, Inc., Santa Clara, CA, USA) with a flame ionization detector to determine the yield of benzaldehyde and 2-nitrovinylbenzene. The piston pump (LC-01P) used in this study was purchased from Jiangshen Technology Co. (Shanghai, China). The compressive strength on the millispheres was measured with a KHKQ-100 particle strength tester (Nanjing Kehe Analytical Instrument Co., Ltd., Nanjing, China). Confocal laser scanning microscopy (CLSM) images were obtained using a Carl Zeiss LSM880 instrument (Carl Zeiss Microscopy GmbH, Jena, Germany). The excitation wavelength of FITC-I was 488 nm (green). The concentration of Rhodamine B in a solution (a mixture of ethanol and water, 1:1 V/V) was 2×10^{-6} M, and the excitation wavelength was 554 nm (red).

3.4. β -Zeolite- NH_2 /SP-Catalyzed Cascade Reactions

3.4.1. Deacetalization–Henry Cascade Reaction over β -Zeolite- NH_2 /SPs in Batch Systems

Briefly, 2 mL of toluene containing acetaldehyde dimethyl acetal (0.10 M) and CH_3NO_2 (0.50 M) was added to a Schlenk tube (10 mL). The catalysts [i. a physical mixture of 30 mg NH_2/SiO_2 SPs (constructed by NH_2/SiO_2 nanoparticle as building block) and 10 mg β -zeolite SPs (constructed by β -zeolite nanoparticle as building block); ii. a physical mixture of 30 mg NH_2/SiO_2 and 10 mg β -zeolite nanoparticles; iii. 40 mg β -zeolite- NH_2 /SPs, prepared with a 1:3 mass ratio of β -zeolite and NH_2/SiO_2 nanoparticles)] were then added into their respective Schlenk tubes and stirred (600 rpm) at 70 °C for the reaction to occur. The Schlenk tubes were allowed to cool to room temperature after reaction. The products were analyzed by GC at intervals. The catalyst was isolated from the reaction mixture via filtration, thoroughly washed with toluene five times, and then dried at 70 °C under a vacuum conditions, thus ready to be used in the next reaction cycle.

3.4.2. Deacetalization–Henry Cascade Reaction over H-Beta-CALB/SPs in Continuous-Flow System

All continuous-flow reactions were performed in a fixed-bed reactor. Briefly, 1.0 g of the β -zeolite- NH_2 /SPs catalyst was uniformly packed into the reactor column, and the catalyst bed was preheated and stabilized to 70 °C prior to the reaction. The mobile phase was prepared by dissolving 0.1 M substrate (benzaldehyde acetaldehyde dimethyl acetal, 4-bromobenzaldehyde dimethyl acetal, or 1-(dimethoxymethyl)-4-methylbenzene) and 0.5 M nitromethane (CH_3NO_2) in toluene. The homogeneous reaction solution was

continuously pumped into the preheated reactor column at a controlled flow rate. During long-term continuous operation, a slight decline in catalytic activity was observed. To maintain high product conversion throughout the reaction process, the pumping flow rate was appropriately adjusted and reduced in a gradual and controlled manner. The effluent from the reactor outlet was collected at regular time intervals and subsequently analyzed by gas chromatography (GC) to monitor reaction performance.

3.5. Product Analysis

The products were analyzed using a gas chromatograph (Agilent GC-7890, Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with an HP-5 capillary column (30 m × 0.32 mm × 0.25 mm) and a flame ionization detector (FID). Nitrogen was used as the carrier gas at a constant flow rate of 24 mL min^{−1}, with the injector and detector temperatures set to 250 °C and 280 °C, respectively. Quantification of benzaldehyde dimethyl acetal, unreacted benzaldehyde dimethyl acetal, and all detected byproducts was carried out using the internal standard method, with *n*-dodecane employed as the internal standard. The calculation formulas for benzaldehyde dimethyl acetal conversion and β-nitrostyrene yield are as follows:

$$\text{Conversion(\%)} = \frac{n_{\text{substrate,initial}} - n_{\text{substrate,final}}}{n_{\text{substrate,initial}}} \times 100\%$$

$$\text{Yield(\%)} = \frac{n_{\text{product}}}{n_{\text{substrate,initial}}} \times 100\%$$

Notes: Substrate—benzaldehyde dimethyl acetal or 1-(dimethoxymethyl)-4-methylbenzene; product—benzaldehyde or β-nitrostyrene.

4. Conclusions

In conclusion, we developed a liquid-marble-templated SP fabrication strategy for a one-pot tandem of incompatible catalytic sites. The key to this strategy is the use of SPs, which spatially compartmentalize incompatible catalytic sites into distinct subcompartments while co-localizing them within a single SP. This unique internal architecture overcomes the long diffusion distances, kinetic mismatch, and low product yields associated with the physical mixing of catalysts, while avoiding the mutual deactivation of active sites caused by direct co-immobilization on a single support. Moreover, our catalysts possess high mechanical strength (3.1 N), allowing them to retain their structural integrity and catalytic stability during long-term continuous-flow operation. As demonstrated by the acid-amine-catalysis deacetalization–Henry cascade reaction, our catalysts exhibit excellent conversion (99%) and yield (75%), with outstanding operational stability (200 h). Overall, this work presents a feasible route for fabricating millimeter-scale tandem catalysts with tunable chemical compositions, controllable active-site distribution and optimized synergistic catalytic performance, which may offer some insights into the design and potential industrial application of incompatible acid–base cascade catalytic systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16100856/s1>. Figure S1. (a) SEM image of NH₂/SiO₂. (b) TEM image of NH₂/SiO₂. (c) SEM image of β-zeolite. (d) TEM image of β-zeolite. Figure S2. (a) FT-IR spectra of mesoporous silica and 3-[2-(2-Aminoethylamino)ethylamino]propyl-trimethoxysilane-modified mesoporous silica. (b) TG curves of mesoporous silica and [2-(2-Aminoethylamino)ethylamino]propyl-trimethoxysilane-modified mesoporous silica. Figure S3. Fluorescence confocal microscopy images of β-zeolite-NH₂/SP catalyst. (a) Amino-modified silica nanospheres are labeled with Rhodamine B. (b) FITC-I-labeled H-beta molecular sieves. (c) H-beta

molecular sieves and NH_2/SiO_2 were labeled, respectively, with FITC-I and Rhodamine B. Figure S4. Time-dependent fluorescence intensity for the transport of Rhodamine B within a β -zeolite- NH_2 /SP catalyst. Figure S5. Recyclability of β -zeolite- NH_2 /SP catalysts. Reaction conditions: 0.2 mmol benzaldehyde dimethyl acetal and 5 equiv. nitromethane, 2 mL toluene, 70 °C. Error bars indicate the standard error from 3 independent experiments. Figure S6. Continuous-flow cascade reaction using 4-bromobenzaldehyde dimethyl acetal as substrate, flow rate from an initial 1.0 mL h^{−1} to 0.8 mL h^{−1} at the end. Reaction conditions: 1.0 g β -zeolite- NH_2 /SPs were packed in a fixed-bed reactor, 0.1 M substrate and 5 equiv. nitromethane in toluene, 70 °C. Error bars indicate the standard error from 3 independent experiments. Figure S7. Results of the cascade of acid-base over β -zeolite SPs and NH_2/SiO_2 SPs in two-stage reactions. Reaction conditions: 0.333 g β -zeolite SPs and 0.666 g NH_2/SiO_2 SPs were packed in a fixed-bed reactor, 0.1 M benzaldehyde dimethyl acetal and 5 equiv. nitromethane in toluene, 70 °C, flow rate from an initial 1.0 mL h^{−1} to 0.8 mL h^{−1} at the end. Reference [52] is cited in the Supplementary Materials.

Author Contributions: X.G. and X.Z. executed the experiments and collected the data; W.L. and Y.Z. contributed by discussing and analyzing the experimental results. X.G. conceived and supervised the project; X.G. wrote the paper. All authors edited the paper. All authors have read and agreed to the published version of the manuscript.

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