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Modulated large-pore mesoporous silica as an efficient base catalyst for the Henry reaction

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Abstract In this study, mesoporous silica materials with tuned pores and surface areas were successfully synthesized by adjusting the amount of applied hexane and controlling the hydrothermal temperature. The synthesized silica materials were then functionalized by an amine group to produce solid base catalysts and be applicable as efficient heterogeneous base catalysts for the Henry reaction. The mesoporous silica catalysts possessing large‑pores and surface area expose their active catalytic sites and thereby improve contacts with reactants fulfilling the reactions expeditiously in comparison with solid base catalysts possessing small‑pores and surface area. The results indicated that the yield of the products is significantly dependent on the structure of the applied solid base catalysts. The modulated large‑pore solid base catalysts presented high catalytic activity in Henry reactions and could be reused for five consecutive cycles.

Keywords Base catalyst · Henry reaction · Heterogeneous catalyst · Mesoporous materials · Nitroaldol condensation · Silica

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Introduction

Nanostructured materials have attracted great interest because of their tunable structures and broad applications [1–5]. Among variable nanostructures, the development of porous nanostructures is an important research area because of their unique physicochemical properties and applicability such as for adsorption, biomedicine, chromatography, catalysis, energy convergence, and gas storage [6–10]. Variable porous nanostructured materials have been applied in catalysis research areas for elevating the efficiency of the catalytic transformations [11–14]. For instance, mesoporous silica and alumina materials have been used as supports for precious nanoparticles (NPs) catalysts due to their low cost, large surface area and porosity, chemical and thermal stability, mechanical strength, and simple synthesis [15–17]. Mesoporous inorganic materials that supported palladium NPs catalysts have expedited various important reactions [18–20]. Another interesting feature of mesoporous silica is the multitude of possible modifications that can be used for easy organics functionalization to present the desired properties [21, 22]. Mesoporous silica materials functionalized with acidic groups (e.g., –COOH, –SO$_3$H, –SH) and/or basic groups (e.g., –NH$_2$, –NRH, –NR$_2$) have been utilized as non-metallic solid catalysts in various reactions such as cascade reactions [23–25]. These heterogeneous catalysts have the benefits of simple recovery and reuse after the accomplishment of reactions and present green chemical processes in comparison to their homogeneous counterparts [26–28]. Although great efforts have been achieved to develop highly stable and sustainable solid acid/base catalysts, there are still major deficiencies with most matrixes needing rectification including available active catalytic sites, catalytic efficiency, and substrates diffusion [29, 30]. In addition, reactants adsorption and interaction with the functional groups in small pore-size supports restrict the effectiveness of these heterogeneous catalysts [31].

The Henry reaction, also known as nitroaldol condensation, is one of the important organic transformations which has been accomplished by inexpensive amine-functionalized mesoporous materials [32–34]. Variable strategies have been investigated to tune the nanostructure of the pores and surface modification of the mesoporous supports for obtaining the desired selective products of this reaction [35]. Different types of amine groups were successfully grafted onto mesoporous silica supports in order to acquire the desired selective products of Henry reactions [36]. To further enhance the catalytic performance of mesoporous silica materials, specific modification of structures with particular open pores can provide readily approachable active catalyst sites; consequently, and facilitate the efficient substrates/products flow yielding products in a short reaction time [37]. If successful, this approach could become generally applicable for base functionalized mesoporous silica catalysts. We therefore envision that synthesizing amine-functionalized mesoporous silica with large pores and surface area will provide accessible active sites and easily interact with reaction media, thus representing the efficient heterogeneous base catalysts for the Henry reaction, which solves many of the aforementioned issues. Herein, we report the modified synthesis of tuned large-

pore mesoporous silica having amine functional groups, and demonstrate its application for the Henry reaction. The active amine functional groups on the high surface area can increase the exposed active sites and thereby improve contact area with reactants fulfilling the heterogeneous Henry reaction efficiently.

Experimental

Materials and characterizations

Water was deionized using a Nano Pure System (Barnsted). The chemicals used in this work were purchased at the highest possible grades. P123 block-copolymer (average $M_n \sim 5800$, PEG, 30 wt%) was purchased from Aldrich. Tetraethylorthosilicate (TEOS, 98%) and hydrogen chloride (HCl 37% concentration) were obtained from Merck and hexane (97%) was purchased from Baker. Transmission electron microscope (TEM) images were obtained using a Philips CM300 microscope at an acceleration voltage of 200 kV. Field emission scanning electron microscopy (FESEM; IROST, MIRALL TESCAN) was used to study the morphology of the synthesized mesoporous materials. The Brunauer, Emmett and Teller surface area (BET), pore volume and pore size distributions were determined using a Barrett, Joyner, and Halenda (BJH) analyzer model (BELLSORP-mini II, BEL, Osaka).

Synthesis of MS70 and MS130 mesoporous silica materials

P123 block-copolymer (4 g) was dissolved in water (30 g) and HCl (120 g, 2 M) solution and stirred for 5 h at 40 °C in a capped bottle. TEOS (9 g) was added into the solution under stirring. The mixture was stirred for 24 h in a capped bottle and then transferred into a Teflon-lined autoclave for further ageing at different hydrothermal temperatures (70 °C for MS70 product and 130 °C MS130 product) for 48 h. All obtained materials were filtered, washed with deionized water, and dried in a vacuo for 10 h. The solids were then calcined at 540 °C for 12 h to remove the remaining surfactant. Final materials were designated as MS70 and MS130, where MS is standing for mesoporous silica, and the numbers are the hydrothermal temperatures applied for the preparation of these two products.

Synthesis of MSH70 and MSH130 mesoporous silica materials

P123 block-copolymer (4 g) was dissolved in water (30 g) and HCl (120 g, 2 M) solution and stirred for 5 h at 40 °C in a capped bottle. Hexane (molar ratio of hexane/P123 = 120) was first mixed with TEOS (9 g) and then added to the solution while stirring. The mixture was further stirred for 24 h in a capped bottle and transferred into a Teflon-lined autoclave for completion of the reactions at different hydrothermal temperatures (70 °C for MSH70 product and 130 °C MSH130 product) for 48 h. All obtained materials were filtered, washed with deionized water, and dried in a vacuo for 10 h. The solids were then calcined at

540 °C for 12 h to remove remaining surfactants. The synthesized materials were designated as MSH70 and MSH130, where MS is standing for mesoporous silica, H implies hexane, and the numbers are the hydrothermal temperatures applied for the preparation of these two products.

Amine-functionalization of mesoporous silica materials

To functionalize the mesoporous silica materials with amine groups, 1 g of each mesoporous silica materials was separately dispersed in vials containing EtOH and stirred at room temperature. Then, (3-aminopropyl) trimethoxysilane (100 µl) was directly added to each mixture vial while vigorous stirring. Finally, 100 µl aqueous ammonia was rapidly added and the mixture vigorously stirred at room temperature for 3 h to obtain amine functionalized mesoporous silica materials. After ageing, the products were filtered, washed several times with ethanol, dried in vacuo and analyzed using a CHNS elemental analyzer.

Heterogeneous Henry/nitroaldol reaction catalyzed by amine-functionalized mesoporous silica catalysts

The Henry reaction was performed using the amine-functionalized mesoporous silica materials as solid base catalysts. Typically, 30 mg of the prepared catalyst was added into a mixture of benzaldehyde (1 mmol) and 5 mL of nitromethane. The reaction mixture was stirred at 90 °C for 3 h.

Results and discussion

In this study, mesoporous silica materials with tuned pores and surface areas were successfully synthesized by adjusting the hexane amount as a swelling agent and controlling the applied hydrothermal temperature. Then, the synthesized mesoporous silica materials were functionalized by an amine group to produce heterogeneous base catalysts. The silica materials synthesized in the absence of swelling agent were designated as MS70 and MS130, where MS is standing for mesoporous silica, and the numbers are the hydrothermal temperatures applied for the preparation of these products. The large-pore mesoporous silica materials synthesized with swelling agent were designated as MSH70 and MSH130, where MS is standing for mesoporous silica, H implies hexane, and the numbers are the hydrothermal temperatures applied for the preparation of these two products.

Figure 1 presents N_2 adsorption–desorption graphs and the corresponding pore size distributions of all four mesoporous materials. MS70 and MS130 mesoporous silica present isotherms of type IV with H1 type hysteresis loops. The isotherms of MSH70 and MSH130 materials can be categorized as type IV according to IUPAC classification. FESEM images of the synthesized mesoporous materials (Fig. 2a–d) indicate that the modification processes including the amine-functionalization step do not cause structural deformation or destruction. TEM studies (Fig. 3a–d) show that the prepared silica materials have well-ordered mesoporous structures with
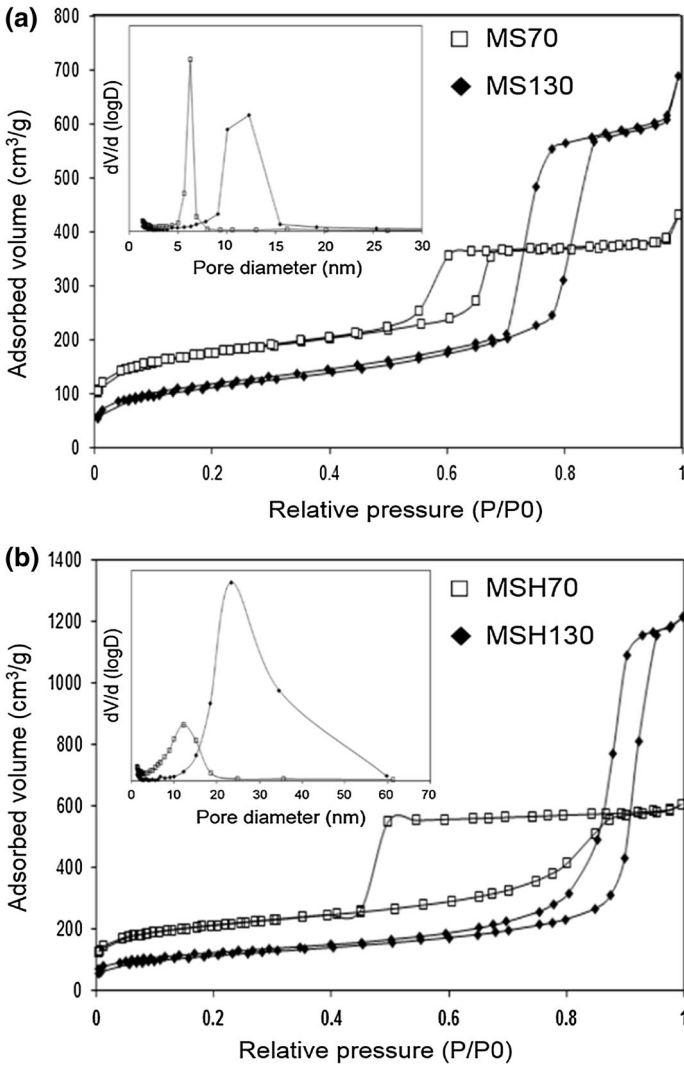
Fig. 1 N_2 adsorption–desorption isotherms of **a** MS70 and MS130 mesoporous silica catalysts and **b** MSH70 and MSH130 mesoporous silica catalysts. The insets show the corresponding pore size diameters

tuned pore channels, which are in good agreement with the results of surface areas and pore sizes comparison studies in Table 1. Accordingly, MSH130 and MS130 catalysts possess pore sizes larger than MS70 and MSH70 while they have smaller surface areas. TEM results indicate that MSH70 and MSH130 catalysts have foam-like structures. In order to prepare mesoporous silica materials as solid base catalysts to expedite the desired reactions, it is important to anchor active amine-functional groups within the support materials by choosing an appropriate organic precursor [38]. Therefore, (3-aminopropyl) trimethoxysilane as a functional amine
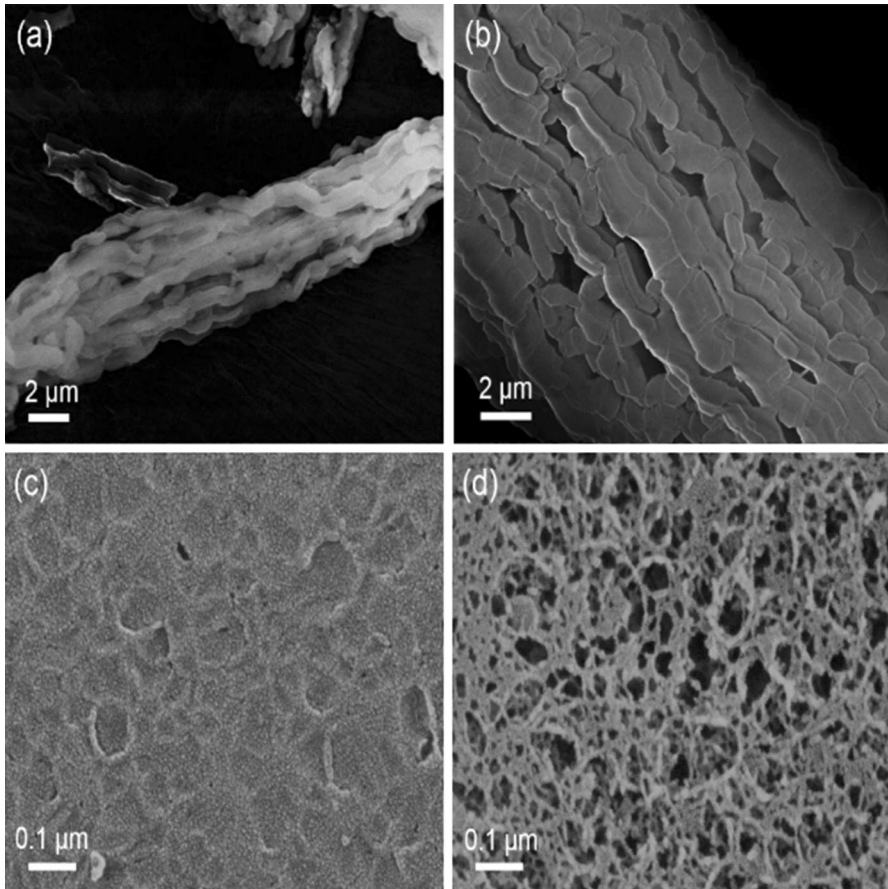
Fig. 2 FESEM images of **a** MS70, **b** MS130, **c** MSH70 and **d** MSH130 mesoporous silica catalysts

was condensed on the mesoporous silica materials to produce solid base catalysts. CHNS elemental analysis provided similar composition of C (9.1%) and N (3.2%) for the prepared amine-functionalized silica catalysts.

It should be noted that two important parameters including pore size and window size regarding foam structures are considered for the detail studies. It is clear that at the lower hydrothermal temperature (70 °C) the small windows structures are formed, while the higher hydrothermal temperature (130 °C) leads to the formation of large windows products. It is noteworthy that the structural properties of heterogeneous catalysts generally affect the efficiency of many transformations [16]. Subsequently, heterogeneous catalysts with high surface area and accessible large-pores to organic reagents accelerate the reaction completion.

The efficiency of the modulated heterogeneous mesoporous silica catalysts with amine functions was compared and verified in the Henry reaction as a prototype reaction. We first investigated the catalytic activity of each catalyst under the identical reaction conditions to find the most efficient catalyst. The results
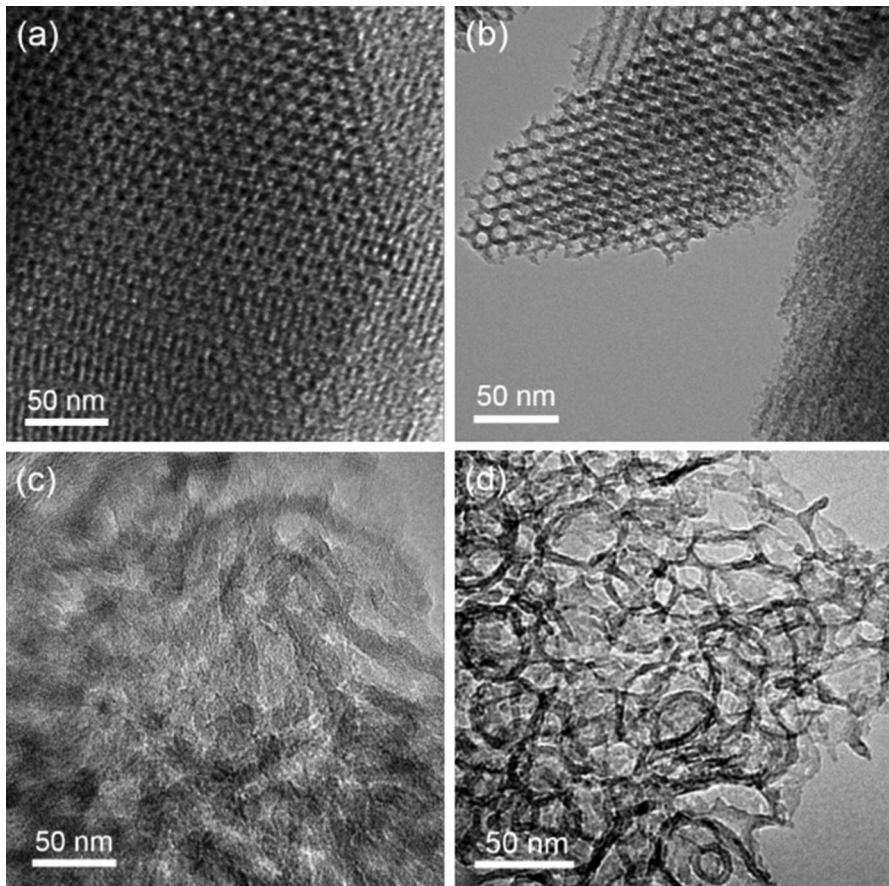
Fig. 3 TEM images of **a** MS70, **b** MS130, **c** MSH70 and **d** MSH130 mesoporous silica catalysts

Table 1 Surface area and pore size of the prepared mesoporous silica materials

Catalyst	Surface area (m^2/g)	Pore size (nm)
MS70	582	4.6
MS130	391	10.9
MSH70	706	5.3
MSH130	396	18.9

elucidated that the yield of the products is significantly dependent on the applied catalysts. MSH130 catalyst provided higher conversion than the other three catalysts. While MSH70 and MS130 catalysts gave similar yields, MS70 produced the least yield (Table 2). The magnificent elevation of the reaction productivity by the MSH130 solid base usage can be described with appropriate surface area and accessible pore diffusion structure of the heterogeneous catalyst. We later expanded

Table 2 Heterogeneous Henry reaction using various mesoporous catalysts
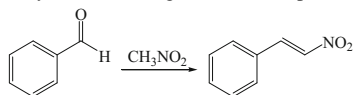
Entry	Catalyst	Yield (%)
1	N/A	–
2	MS70	67
3	MS130	79
4	MSH70	80
5	MSH130	98

Reaction conditions: benzaldehyde (1 mmol), nitromethane (5 mL), catalyst (30 mg), 90 °C, 3 h

Table 3 Heterogeneous Henry reaction catalyzed by MSH130 solid base

Entry	Substrate	Product	Yield (%)
1			98
2			85
3			80
4			72

Reaction conditions: substrate (1 mmol), nitromethane (5 mL), MSH130 catalyst (30 mg), 90 °C, 3 h

the breadth of the substrates in the heterogeneous Henry reaction catalyzed by the MSH130 solid base, which were accomplished successfully (Table 3).

Reusability of heterogeneous catalysts is very important for industrial applications. Therefore, we verified the recycling and reuse of the modulated MSH130 solid base catalyst in the Henry reaction, which was successfully recycled and reused for five consecutive cycles of benzaldehyde (Table 4).

Table 4 Recycling of MSH130 solid base catalyst in the Henry reaction

Cycle	1st	2nd	3rd	4th	5th
Yield (%)	98	95	94	93	92

Reaction conditions: benzaldehyde (1 mmol), nitromethane (5 mL), MSH130 catalyst (30 mg), 90 °C, 3 h

Conclusions

In conclusion, we prepared mesoporous silica materials with tunable pores and surface areas by controlling the amount of hexane and hydrothermal temperature. The prepared mesoporous silica materials could be easily functionalized by amine group to be utilized as retrievable solid base catalysts for heterogeneous Henry reactions. The modulated framework possesses large-pores with active amine functional groups on its high surface area; thus, this enhances the exposed active catalyst sites and contacts with reactants accelerating the reaction completion efficiently. The designed large-pore solid base catalyst could be reused for five consecutive cycles in nitroaldol condensation of benzaldehyde.

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