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#### Short Communication

# Controllable acid-base bifunctionalized mesoporous silica: Highly efficient catalyst for solvent-free Knoevenagel condensation reaction

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#### A R T I C L E I N F O

#### ABSTRACT

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#### 1. Introduction

Development of well-defined catalytic sites and exploration of cooperative catalysis have attracted a great deal of interest due to their high efficiency in organic synthetic chemistry [1]. One common strategy to study cooperative catalysis is to employ a supporting material [2], in which different functionalities can be assembled onto this material and well-defined catalytic microenvironment can be controlled. Such a strategy does not only solve the problem of catalyst recycling, but also does improve the catalytic activity via cooperative catalysis of different functionalities. Mesoporous silica as a kind of ideal supporting materials shows some salient features [3]. Besides general advantages of large surface area and regular pore structure. some mesoporous silica prepared by a co-condensation method can allow to load different types of functionalities and to control their uniform distribution onto pore surfaces [4,5]. Recently, some of mesoporous materials have been used successfully to explore bifunctional cooperativity in a variety of catalytic reactions [6–14].

Knoevenagel condensation as an important carbon – carbon bond forming reaction is commonly used to evaluate both organic [15] and inorganic [16] basic catalysis. In particular, some demonstrations about acid-base cooperativity have also been appeared in the literatures. The pioneering work reported by Hein group [17] found that there was an acid-base cooperativity when a weakly basic resin with an additive of acetic acid was employed as a bifunctional catalyst.

A controllable acid-base bifunctionalized mesoporous catalyst with acidic sites and basic sites in adjacent arrangements was prepared *via* an *in situ* cleavage of sulfonamide bond on synthetic process. During Knoevenagel condensation reaction of aromatic aldehydes and ethyl cyanoacetate under microwave irradiation in solid media, the mesoporous bifunctionalized catalyst Me-A/B-SBA-15 exhibited higher catalytic activity than those of the corresponding amine-functionalized catalyst and the randomly-arranged acid-base catalyst, showing obvious acid-base cooperativity.

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Kubota group [18] reported that an organic cationic-MCM-41 composite showed higher activity than that of organic cation due to acid-base cooperativity. Recently, some mesoporous silicas for the investigation of acid-base cooperativity have also been explored. Angeletti group [19] expatiated a silanol act as an acidic site and 1,8bis(dimethylaminonaphthalene) functional group immobilized onto MCM-41 material act as a basic site in acid-base cooperativity. In particular, Shanks group and Katz [20,21] explored cooperative primary amine mechanism of acid-base cooperativity through employing an aminopropyl-functionalized SBA-15 mesoporous silica. Although the fruitful achievements have been obtained in this research field, however, these bifunctional groups onto supports distribute randomly and lack of a continuous arrangement of acidic and basic sites. There is a question whether bifunctional groups onto materials do reflect truly the nature of cooperative catalysis. Therefore, an innovative strategy to control independent acid and base sites in adjacent arrangement and to match equivalent mole relationship onto materials is helpful to elucidate the nature of acidbase cooperativity.

Recently, we have reported a series of mesoporous catalysts and their applications in catalytic processes [22,23]. Herein we develop a synthesis of mesoporous acid-base bifunctionalized catalyst *via* a cocondensation method, and apply it to microwave-promoted Knoevenagel condensation reaction in solid medium. The key feature is that arylsulfonated amide silica resource is separated on an *in situ* synthetic process to keep acid and base sites in adjacent arrangements onto mesoporous materials. The research focuses on as follows: (1) construction of a mesoporous well-defined acid-base bifunctionalized catalyst; (2) investigation of synergistical effect of acid-base cooperativity in Knoevenagel condensation reaction.

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#### 2. Experimental

#### 2.1. Preparation of acid-base bifunctionalized catalyst Me-A/B-SBA-15 (5)

Under argon atmosphere, a suspension of A/B-SBA-15 (4) (1.00 g) and HMDS [(CH<sub>3</sub>)<sub>3</sub>Si)<sub>2</sub> N] (5 mL, 0.025 mol) in 25 mL of dry THF was stirred overnight. The mixture was filtered through filter paper and rinsed with excess acetone. The collecting solids were then suspended again in 20 mL dry THF and 0.74 g of *t*-BuOK (6.70 mmol) was added. The mixture was allowed to reflux for 6 h. After cooling to room temperature, the pH value of suspension was adjusted to 7.0 using acetic acid. Finally, the suspension was filtered and rinsed with excess ethanol. The collecting solids were dried under vacuum at 60 °C for 6 h to afford Me-A/B-SBA-15 (5) (1.06 g) in the form of a paler white powder. IR (KBr) cm<sup>-1</sup>: 3043 (w), 2962 (w), 2898 (w), 1597 (w), 1088 (s), 947 (m), 801 (w), 557 (w), 465 (m); Elemental analysis (%): C 24.58, H 4.176, N 0.747, S 1.707; d<sub>pore</sub>: 5.4 nm; S<sub>BET</sub>: 532 m<sup>2</sup>/g; <sup>29</sup>Si MAS NMR (79.5 MHz):  $Q^4$  ( $\delta = -110.4$  ppm),  $Q^3$  ( $\delta = -101.3$  ppm),  $T^{3} (\delta = -68.6 \text{ ppm}); {}^{13}\text{C CP MAS NMR} (100.6 \text{ MHz}); 127.7, 56.9, 41.6,$ 27.4, 20.3, 15.1, 8.1, 0.5 ppm.

#### 2.2. Characterizations

The X-ray powder diffraction (XRD) experiments were carried out on a Rigaku D/Max-RB diffractometer with Cu K $\alpha$  radiation. Transmission electron microscopy (TEM) studies were performed on a JEOL JEM2010 electron microscope, operated at an acceleration voltage of 200 kV. Fourier transform infrared (FTIR) spectra were collected with a Nicolet Magna 550 spectrometer by using the KBr method. Nitrogen adsorption isotherms were measured at 77 K with a Quantachrome Nova 4000 analyzer. The samples were measured after being outgassed at 423 K overnight. Pore size distributions were calculated by using the BJH model. The specific surface areas (SBET) of samples were determined from the linear parts of BET plots ( $p/p_0$ =0.05–1.00). Solid-state <sup>29</sup>Si MAS NMR and <sup>13</sup>C CP MAS NMR spectra were recorded at 79.5 and 100.6 MHz, respectively, using a Bruker AV-400 spectrometer.

#### 2.3. Catalytic reaction

A typical procedure was as follows: Aldehyde (2.0 mmol) and ethyl cyanoacetate (0.24 mL, 2.20 mmol) and Me-A/B-SBA-15 (5) (60.0 mg, 32.0 µmol, based on Elemental analysis) were added to a thick walled Pyrex tube. When the addition was complete, the tube was positioned in a MAS-2 single mode cavity microwave with a water-cooled condenser from Sineo Microwave Chemistry Technology (China) Co. LTD, adjusting the reaction temperature button at 100 °C and producing continuous irradiation at 2.45 GHz. The mixture was irradiated in 700 W for 10 min. After being cooled down to room temperature, 2.0 mL of ethyl acetate was then added and the mixture was filtrated. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was further purified by flash column chromatography on silica gel (eluent: ethyl acetate/hexane = 1:1) to afford a mixture of aldehydes and the corresponding product, which was used to determine conversion and selectivity via a comparison of concentration of start materials using a HPLC analysis with a UV-vis detector containing a shim-pack VP-ODS column (  $\Phi$  4.6×150 mm) (refer to Fig. S5 in the supporting information).

#### 3. Results and discussion

3.1. Synthesis of the acid-base bifunctionalized catalyst Me-A/B-SBA-15 (5)

The mesoporous bifunctionalized catalyst, abbreviated as Me-A/B-SBA-15 (**5**), was prepared by a co-condensation approach as shown in

Scheme 1. Firstly, the reaction 3-aminopropyltrimethoxysilane (1) of 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (2) using Et<sub>3</sub>N as abasic reagent gave N-trimethoxysilylpropyl-(4-trimethoxysilylethyl) benzenesulfonamide (3) with 56% isolated yield (See supporting information). The condensation N-trimethoxysilylpropyl-(4-trimethoxysilylethyl)benzenesulfonamide (3) with Si(OEt)<sub>4</sub> was then carried out to afford A/B-SBA-15 (4) as a white powder (See supporting information) according to reported method [23]. Finally, after the protection of silicon-hydroxyl groups of A/B-SBA-15 (4) with trimethysilvl groups [24], the resulting rude products were treated with excess potassium tert-butoxide followed by control of pH to afford catalyst Me-A/B-SBA-15 (5) as a paler white powder. In order to clarify when cleavage of sulfonamide silica resource occurred, the control experiment using the parent N-propyl-toluenesulfonamide as a starting material was carried out. The result showed that N-propyl-toluenesulfonamide was rather stable in 2 N hydrochloric acid at 40 °C, even no cleavage occurred in refluxed condition. This demonstrated no cleavage occurred on prepared process of A/B-SBA-15 (4). However, quantitative cleavage products were obtained when 10 equivalent of *t*-BuOK was used as a cleavage reagent [25]. This behavior indicated that the cleavage of sulfonamide silica resource occurred on last step, resulting in an adjacent arrangement of an acidic site and a basic site onto materials. Elemental analysis of Me-A/B-SBA-15 (5) calculated from mass% of N (0.747%) and S (1.707%) further confirmed that the mole ratio of sulfur

# 3.2. Structural and morphological properties of A/B-SBA-15 ( $\mathbf{4}$ ) and Me-A/B-SBA-15 ( $\mathbf{5}$ )

to nitrogen was 1:1. The thermal gravimetric datum (see Fig. S3 in

supporting information) indicated 32% organic molecules were loaded

onto the mesoporous materials, which was consistent with the data of

Elemental analysis.

The incorporation of organic acid and base groups onto the mesoporous materials could be confirmed by solid-state NMR spectra. As shown in Fig. 1(a), the <sup>29</sup>Si MAS NMR spectra of A/B-SBA-15 (4) and Me-A/B-SBA-15 (5) showed two groups of signals with four oxygen neighbors (Q-type species) originated from TEOS and with three oxygen neighbors (T-type species) derived from silvlether groups. Typical isomer shift values were -91.5/-101.5/-110 ppm for  $Q^2/Q^3/Q^4$ signals  $(Q^{2}{(HO)_{2}Si(OSi)_{2}}, Q^{3} {(HO)Si(OSi)_{3}}, Q^{4} {Si(OSi)_{4}})$  and -48.5/-58.5/-67.5 ppm for T<sup>1</sup>/T<sup>2</sup>/T<sup>3</sup> signals (T<sup>1</sup>{R(HO)<sub>2</sub>SiOSi}, T<sup>2</sup> {R (HO)Si(OSi)<sub>2</sub>}, T<sup>3</sup> {RSi(OSi)<sub>3</sub>}) [26]. A/B-SBA-15 (**4**) gave a medium Q<sup>4</sup> (-112.2 ppm), a strong Q<sup>3</sup> (-102.8 ppm), a weak Q<sup>2</sup> (-92.5 ppm), a medium  $T^3$  (-67.4 ppm) and a weak  $T^2$  (-58.9 ppm) peak. Me-A/B-SBA-15 (5) presented a strong  $Q^4$  (-110.4 ppm), a medium  $Q^3$ (-101.3 ppm) and a weak T<sup>3</sup> (-68.6 ppm) peak. As compared with A/B-SBA-15 (**4**), the enhanced  $Q^4$  signal and disappeared  $Q^2$  signal in Me-A/B-SBA-15 (5) suggested that the catalyst 5 possessed mainly network structure of {Si(OSi)<sub>4</sub> and (HO)Si(OSi)<sub>3</sub>} while the enhanced T<sup>3</sup> signal and the disappeared T<sup>2</sup> signal indicated the formation of {RSi  $(OSi)_3$  (R = organic acid and base groups) as a part of wall in mesoporous structure. The <sup>13</sup>C CP/MAS NMR spectra displayed the peaks at 127.6 (C-Ph), 68.9 (-OCH<sub>2</sub>CH<sub>3</sub>), 41.6 (-CH<sub>2</sub>NH<sub>2</sub>), 27.4  $(-CH_2Ph)$ , 20.3  $(-CH_2CH_2NH_2)$ , 15.1  $(-OCH_2CH_3)$ , 8.1  $(-CH_2Si)$ , 0.5 (-CH<sub>3</sub>Si) ppm in the Me-A/B-SBA-15 (5) and 127.6 (C-Ph), 69.6 (-OCH<sub>2</sub>CH<sub>3</sub>), 42.1 (-CH<sub>2</sub>NH<sub>2</sub>), 27.7 (-CH<sub>2</sub>Ph), 20.4 (-CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>), 14.8 (-OCH<sub>2</sub>CH<sub>3</sub>), 8.3 (-CH<sub>2</sub>Si) ppm in the A/B-SBA-15 (4), corresponding to aromatic and aliphatic carbon atoms as marked in Fig. 1(b).

The powder XRD patterns (Fig. 2) revealed that both A/B-SBA-15 (**4**) and Me-A/B-SBA-15 (**5**) exhibited one similar intense  $d_{100}$  diffraction and two similar weak  $d_{110}$  and  $d_{200}$  diffractions, implying that the ordered dimensional-hexagonal mesostructure (*p6mm*) observed in pure SBA-15 [22] could be well preserved after the co-condensation and the protection [27]. The TEM morphologies further confirmed that both A/B-SBA-15 (**4**) and Me-A/B-SBA-15 (**5**) had



Scheme 1. Synthesis of the acid-base bifunctionalized catalyst 5.



Fig. 1. NMR spectra of 4–5. (a) <sup>29</sup>Si MAS NMR and (b) <sup>13</sup>C CP MAS NMR.

well-ordered mesostructures with the dimensional-hexagonal arrangements as shown in Fig. 3. Nitrogen adsorption-desorption isotherms of A/B-SBA-15 (**4**) and Me-A/B-SBA-15 (**5**) (Fig. 4) exhibited typical IV type nitrogen adsorption-desorption isotherms with H<sub>1</sub> hysteresis loop and a visible step at  $P/P_0 = 0.50-0.85$ , corresponding to capillary condensation of nitrogen in mesopores. In comparison with A/B-SBA-15 (**4**), Me-A/B-SBA-15 (**5**) presented a decrease in the nanopore size, surface area, and pore volume. This behavior suggested that the occupation of trimethysilyl groups onto the pore channels made the pores narrower, resulting in an increase of the wall thickness [22].



Fig. 2. Powder XRD patterns of 4-5.



Fig. 3. TEM images of 4-5 viewed along [100] and [001] directions.

3.3. Microwave-promoted Knoevenagel condensation of aromatic aldehydes and ethyl cyanoacetate

Microwave-assisted catalysis as a convenient method [28] can accelerate obviously catalytic reactions from hours or days to minutes, which "solvent-free" catalytic processes can match the need of green environment [29]. Recently, employing both strategies for Knoevenagel condensation reaction of aromatic aldehydes and ethyl cyanoacetate had appeared in the literature [30-32]. Shown in Table 1 was Knoevenagel condensation reaction of aromatic aldehydes and ethyl cyanoacetate performed under microwave radiation in solid medium, where for each reaction a mixture of each aromatic aldehyde and 1.1 equivalent of ethyl cyanoacetate and a certain amount catalyst was irradiated for 10 min at 100 °C under ambient pressure using a power setting of 700 W. When the catalyst Me-A/B-SBA-15 (5) with the same loading-amount amino functionality was employed according to the literature [20,21], it was found that ethyl (E)-2-cyano-3-phenyl-2-propenoate was obtained quantitatively. GC-MS analysis showed that only one well-separated GC peak was observed, suggesting that only E isomer of the products was formed [33]. Such a reaction yield was obviously higher than those without the microwave irradiation [20,21,30,31], even higher than that with the microwave irradiation [32]. As shown in entry 1, when the mole ratio of catalyst/substrate was down to 1.6%, the catalyst Me-A/B-SBA-15 (5) still gave the corresponding product with 91.0% conversion. On the basis of the about excellent result, the catalyst Me-A/B-SBA-15 (5) was further investigated using a variety of aromatic aldehydes as substrates (entries 2-8). In general, a variety of aromatic aldehydes were reacted smoothly with ethyl cyanoacetate to afford the



Fig. 4. Nitrogen adsorption-desorption isotherms of 4-5.

corresponding products with high yields. No by-products and the corresponding isomers were observed confirmed by HPLC, in which only one well-separated HPLC peak was observed. The highly catalytic efficiency observed here should be due to the acid-base cooperativity discussed below [20].

To gain better insight into the effect of acid-base cooperativity, three control experiments were carried out using unsilvlated NH<sub>2</sub>-SBA-15, unsilvlated A/B-SBA-15 (4) and silvlated Me-NH<sub>2</sub>-SBA-15 as catalysts under the similar reaction conditions when 4-methylbenzaldehyde was chosen as a substrate. It was found that the reaction using unsilylated NH<sub>2</sub>-SBA-15 and A/B-SBA-15 (4) as catalysts gave ethyl (E)-2-cyano-3-(4-methyl)phenyl-2-propenoate with high conversion as nearly same as the catalyst Me-A/B-SBA-15 (5) (entries 9-10 versus entry 7), while that of using silvlated Me-NH<sub>2</sub>-SBA-15 as a catalyst afforded the corresponding product with 55.8% conversion (entry 11). High activities in the former suggested that both NH<sub>2</sub>-SBA-15 and A/B-SBA-15 (4) had an acid-base cooperativity, in which silanol onto NH<sub>2</sub>-SBA-15 [20,21] or sulfonic acid group onto A/B-SBA-15 (4) acted as an acidic site in cooperative catalysis. The lower activity in the latter indicated that the absence of silanol as an acidic site located on close proximity of basic site resulted in a loss of acid-base cooperativity, which only underwent basic catalysis. Such a behavior could be further proved by the physical mixture of Me-NH<sub>2</sub>-SBA-15 plus SO<sub>3</sub>H-SBA-15 as a bifunctionalized catalyst in the literatures and our experimental result (entry 12) [34,35]. In order to further prove truly cooperative catalysis in Me-A/B-SBA-15 (5), the control experiment employing silvlated NH<sub>2</sub>-SBA-15/SO<sub>3</sub>H-SBA-15 (a random distribution of acidic and basic sites onto materials) [14] as an acid-base bifunctionalized catalyst was also carried out under the similar reaction conditions. It was found that only 82.4% conversion was obtained (entry 13). Apparently, the silvlated NH<sub>2</sub>-SBA-15/SO<sub>3</sub>H-SBA-15 presented a lower reactivity than Me-A/B-SBA-15 (5) and higher reactivity than Me-NH<sub>2</sub>-SBA-15. Such a result suggested that there was the part of acid-base cooperativity, in which the parts of amino groups and sulfonic groups were in adjacent arrangements because the acid and base functionalities were randomly-arranged on mesoporous materials.

#### 4. Conclusion

In conclusion, we supplied a facile approach to prepare the mesoporous silica-supported acid-base bifunctionalized catalyst Me-A/B-SBA-15 (**5**). The bifunctionalized catalyst exhibited excellent catalytic activity in solvent-free Knoevenagel condensation under microwave irradiation, which was obviously higher than that of the corresponding amine-functionalized catalyst Me-NH<sub>2</sub>-SBA-15, even than that of the randomly-arranged acid-base catalyst. Such behavior was originated from an acid-base cooperativity, in which a sulfonic acid group could activate substrate and a primary amine group could catalyze Knoevenagel condensation reaction.

#### Table 1

Microwave-promoted Knoevenagel condensation of aromatic aldehydes and ethyl cyanoacetate.<sup>a</sup>



Entry	Substrate	Catalyst	Conversion (%) <sup>b</sup>	Yield (%) <sup>c</sup>
1	7	5	91.0	86
2	8	5	97.1	92
3	9	5	96.5	91
4	10	5	99.5	94
5	11	5	98.2	93
6	12	5	92.2	89
7	13	5	97.9	93
8	14	5	91.6	87
9	13	4	95.5	93
10	13	NH <sub>2</sub> -SBA-15	94.6	91
11	13	Me-NH <sub>2</sub> -SBA-15	55.8	50
12	13	Physical mixture <sup>d</sup>	49.5 <sup>d</sup>	47 <sup>d</sup>
13	13	Bifunctional catalyst <sup>e</sup>	82.4 <sup>e</sup>	79 <sup>e</sup>

<sup>a</sup> Reactions were carried out using a MAS-2 single mode cavity microwave with a water-cooled condenser (continuous irradiation: 2.45 GHz, power: 700 W). Reaction conditions: catalyst (60.0 mg, 32.0 µmol, based on Elemental analysis), aromatic aldehyde (2.0 mmol), ethyl cyanoacetate (2.2 mmol), reaction time 10 min, and reaction temperature 100 °C. <sup>b</sup> HPLC conversion.

<sup>c</sup> Isolated yield (<sup>1</sup>H-NMR Spectra of products refer to supporting information in Fig. S4).

- Data was obtained using physical mixture of Me-NH<sub>2</sub>-SBA-15 plus SO<sub>3</sub>H-SBA-15 [14] as a catalyst.
- <sup>e</sup> Data were obtained using the randomly-arranged silvlated NH<sub>2</sub>-SBA-15/SO<sub>3</sub>H-SBA-15 [14] as an acid-base bifunctional catalyst.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.catcom.2011.08.004.

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