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The effect of the distance between acidic site and basic site immobilized on mesoporous solid on the activity in catalyzing aldol condensation

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ABSTRACT

Acid–base bifunctional heterogeneous catalysts containing carboxylic and amine groups, which were immobilized at defined distance from one another on the mesoporous solid were synthesized by immobilizing lysine onto carboxyl-SBA-15. The obtained materials were characterized by X-ray diffraction (XRD), N_2 adsorption, Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron micrographs (SEM), transmission electron micrographs (TEM), elemental analysis, and back titration. Proximal-C-A-SBA-15 with a proximal acid–base distance was more active than maximum-C-A-SBA-15 with a maximum acid–base distance in aldol condensation reaction between acetone and various aldehydes. It appears that the distance between acidic site and basic site immobilized on mesoporous solid should be an essential factor for catalysis optimization.

1. Introduction

Surface-modified mesoporous materials with various active sites have been extensively investigated in recent years for catalysis [1–4], chemical sensing [5], separation [6,7], and nanoscience [8,9]. Many monofunctionalized mesoporous silica catalysts have been demonstrated to have unique properties [10–15]. However, as for many applications, bifunctional or multifunctional mesoporous silica catalysts are much more desirable [16–25], since the combined functionalities may act in a cooperative way to improve the reactivity of the catalysts. Much attention has been paid to the combination of organic functional groups, bifunctionalized mesoporous silica nanosphere materials with ureidopropyl group and 3-[2-(2-aminoethylamino)ethylamino]-propyl group [24], or with amine groups and thiols [25]. Zeidan et al. have reported a cooperative effect of SBA-15 containing sulfonic acid and thiol, which exhibits a cooperative effect in a condensation reaction [19]. Dufaud and Davis have reported multifunctional heterogeneous SBA-15 containing primary amine and different acid centers (benzenesulfonic acid, phosphoric acid, or carboxylic acid) [20,21].

Interest in bifunctional catalysts synthesized by controlling spatial arrangement of the functional groups has been growing recently. Site isolation is an effective method to control the distance between functional groups. Our group has reported two acid–base bifunctional mesoporous materials Benzyl-APS-S-SBA-15 and Anthracyl-APS-S-SBA-15 by controlling steric hindrance [26]. Alauzun et al. [27] and Lu et al. [28] have also reported on bifunctionalized mesoporous materials containing an acidic site and a basic site isolated from one another. In addition, bifunctional groups in pairs may be beneficial to achieve cooperative effect. Davis et al. have synthesized acid/thiol paired catalysts involving the design of an organosilane precursor [29,30]. Also, Katz and Bass developed a method to synthesize the thiol/amine paired catalysts based on a xanthate protection strategy to control thiol/amine distance [31].

As reported previously, acid–base cooperative catalysis has been involved in various reactions such as Michael addition [16], aldol condensation [20–22], Henry condensation [16], and Knoevenagel condensation [16,32,33]. The reactions may be focusing on the cooperative action of acid–base groups by the simultaneous activation of both electrophilic and nucleophilic reaction partners. In addition, the amino acids themselves contain carboxylic and amine groups, and they have been used as catalysts in condensation reaction. For example, proline and its derivatives have been proven to be the superior catalysts in the aldol condensation reaction [34–36]. Córdova et al. have also reported that linear amino acids and their derivatives act as catalysts for aldol condensation reaction [37]. However, no report of the linear amino acids that are anchored on solid to perform acid–base cooperative catalysis has appeared.

In this paper, we made an attempt to immobilize different amine group of lysine on mesoporous silica for the synthesis of carboxyl/amine paired catalysts. The carboxylic/amine distance was defined onto the backbones of the mesoporous silica. Moreover, how the distance between active sites effected the catalytic activity was explored based on these newly developed materials.

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2. Material and methods

2.1. Materials

Pluronic123 (Aldrich), HCl (A.R), 4-nitrobenzaldehyde (Acros), 4-(trifluoromethyl)benzaldehyde (Acros), 4-cyanobenzaldehyde (Acros), acetone (A.R), tetraethyorthosilicate (TEOS) (Aldrich), 2-Cyanoethyltriethoxysilane (CTES) (Gelest), H_2SO_4 (A.R), triethylamine (A.R), dimethyl sulfoxide (DMSO) (A.R), and boc-lys-OMe · HCl (Aladdin), H-lys (boc)-OMe · HCl (Aladdin), *N*-ethyl-*N*-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) (Aladdin), and *N*-hydroxysuccinimide (NHS) (Aladdin) were commercially available and used as received.

2.2. Methods

2.2.1. Preparation of carboxyl-SBA-15 (SBA-15-COOH)

The carboxyl-SBA-15 sample was prepared according to literature procedure [14,15]. In a typical synthesis, 2-cyanopropyltriethoxysilane (CTES) was introduced to a hydrochloric acid solution of the triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$). After hydrolyzed for 50 min under stirring at 40 °C, tetraethoxysilane (TEOS) was added into the mixture slowly. The molar composition of the mixture was $(1-x)$ TEOS:x CTES:0.017 P123:5.9 HCl:193 H_2O, where $x=0.075$. Next, the resultant mixture was stirred at 40 °C for 20 h, followed by aging at 100 °C for 24 h under static condition. The solid product was recovered by filtration and dried at 60 °C. For removal of the template and hydrolysis of the –CN groups, the dried product was treated with 48.0% H_2SO_4 solution at 95 °C for 24 h. Subsequently, the product was recovered by washing with water until the eluent became neutral, and finally dried at 90 °C to obtain SBA-15-COOH.

2.2.2. Preparation of Pro-proximal-C-A-SBA-15

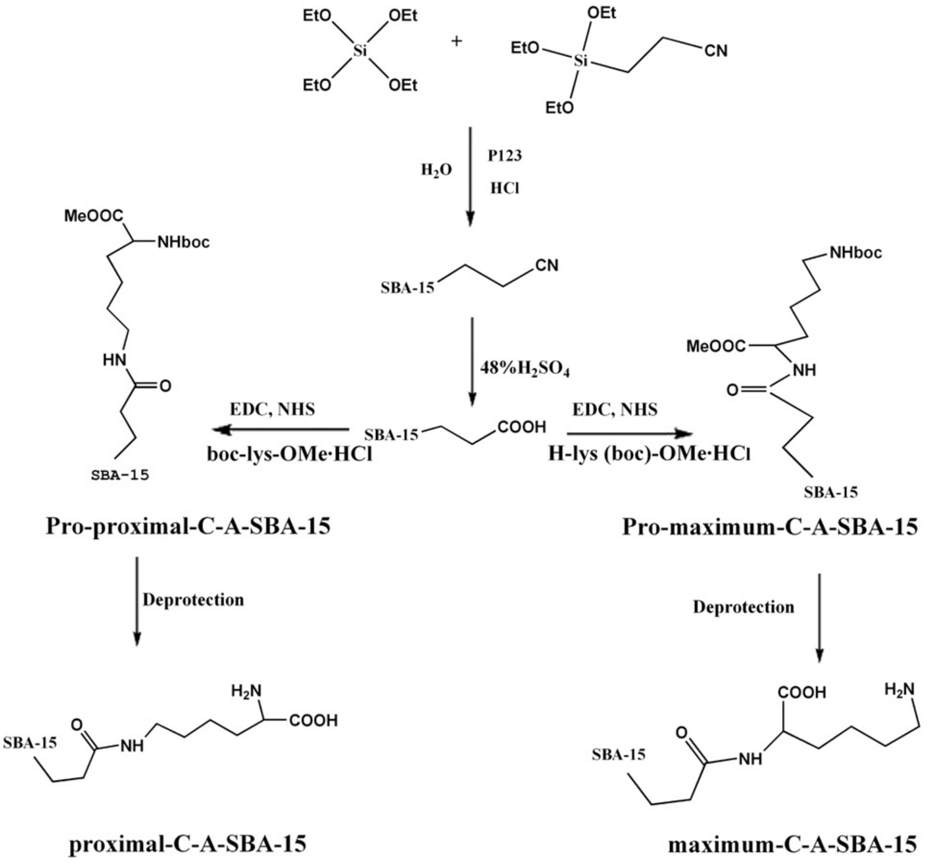
Pro-proximal-C-A-SBA-15 was prepared by activating carboxyl-SBA-15 with *N*-hydroxysuccinimide (NHS), using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) as coupling agent. The 0.5 g boc-lys-OMe · HCl (Excess) was dispersed in 10 ml deionized water, and aqueous 0.19 g NHS and 0.31 g EDC were mixed with 1.2 g SBA-15-COOH/dimethyl sulfoxide (DMSO) solution [38]. Finally, the two solutions were mixed and the pH was adjusted to 8 using triethylamine. The mixture was stirred vigorously at 38 °C for 8 h, and then centrifuged and washed several times with ethanol and copious amount of water. The prepared material with protected groups and proximal carboxylic/amine distance was termed Pro-proximal-C-A-SBA-15 (Scheme 1).

2.2.3. Preparation of Pro-maximum-C-A-SBA-15

Pro-maximum-C-A-SBA-15 with protected groups and enlarged carboxylic/amine distance was synthesized in a similar manner to Pro-proximal-C-A-SBA-15, except that H-lys (boc)-OMe · HCl was used instead of boc-lys-OMe · HCl (Scheme 1).

2.2.4. Preparation of proximal-C-A-SBA-15 and maximum-C-A-SBA-15

After drying the materials of Pro-proximal-C-A-SBA-15 and Pro-maximum-C-A-SBA-15, we deprotected the side chains by shaking in 94% trifluoroacetic solution (water 5% (v/v), triisopropylsilane 1% (v/v)) for 3 h [39]. The solids were collected by filtration with plenty of water and ethanol to give the samples termed proximal-C-A-SBA-15 and maximum-C-A-SBA-15, respectively (Scheme 1).



Scheme 1. Synthesis of proximal-C-A-SBA-15 and maximum-C-A-SBA-15.