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Acid–base cooperativity in condensation reactions with functionalized mesoporous silica catalysts

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ABSTRACT

The Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate was used to test the acid–base cooperativity of SBA-15 mesoporous silica co-condensed with aminopropyl groups as well as silica co-condensed with dihydroimidazole groups. Surface silanols were capped with trimethylsilyl groups using hexamethyldisilazane to determine the effects of the silanol groups on catalytic activity. The activities of the mesoporous silicas with or without capped silanols were compared to the activity of propylamine free in solution. Silylation resulted in a significant loss of activity, where turnover frequencies dropped nearly to those of the homogeneous base. The same behavior was also observed with dihydroimidazole-functionalized SBA-15, which catalyzes the Knoevenagel condensation by a different mechanism. Not only did these results indicate cooperative effects in heterogeneous systems, but cooperativity between a homogeneous base and silanols on unfunctionalized SBA-15 was also observed to a lesser extent. These results demonstrated that acid–base cooperativity seen in well-defined single sites can also be demonstrated on an extended catalytic domain on the surface of mesoporous silica where the active sites are not rigorously isolated.

1. Introduction

Many enzymes catalyze reactions by employing acid–base pairs within their active sites. Studies by Bass et al. [1–3] copied this acid–base cooperativity by creating well-defined catalytic sites within silica, synthesized via an imprinting method [4]. Using the Knoevenagel condensation reaction, they demonstrated acid–base cooperativity between silanol and aminopropyl groups within single sites. An important question is whether these isolated site results can be extended to catalysts with higher surface areas while maintaining the catalytic cooperativity. Additionally, to distinguish the role of the silanols as weak acids from the effect of the hydrophilicity or hydrophobicity of the catalyst surface, the effect of solvent on catalytic activity needs to be investigated. Another point of interest is whether the use of a base that operates via a different mechanism will attain the same cooperative effects. The work described here examines the extension of the single site work performed by Bass et al. to functionalized mesoporous silica where co-condensed catalytic sites exist on extended surfaces.

The ability to achieve cooperative catalysis with functionalized mesoporous silica has recently been reported by Zeidan et al. [5,6] in aldol condensation reactions. The cooperative effects were observed between sulfonic acid and thiol groups and sulfonic acid and amine groups. A recent study by Motokura et al. [7] with amine-grafted amorphous silica–alumina used in three carbon–carbon bond forming reactions was similar to the study performed by Bass and coworkers. However, the support in the Motokura paper contained stronger Brønsted acids than the silica silanols and additionally included testing of homogeneous amines as well as mixtures of the unfunctionalized support and homogeneous amines. A limitation of that particular study was that it did not systematically investigate support–active site cooperativity via the removal of the support component from an otherwise bifunctional system, which is addressed in the current work through silylation of the surface silanols. Additionally, the silica–alumina support lacked an ordered pore structure and the amines were grafted onto the surface, limiting the extension of these results to the design of a controlled catalytic domain in mesoporous silica.

Functionalization of mesoporous silica by co-condensation has the advantages of controllable loadings and more extensive distribution throughout pore surfaces over the alternative method, functionalization by grafting [8]. Co-condensed mesoporous silica has extended pore wall surfaces that can serve as an uniform catalytic domain whereas silica gel can contain sites with limited accessibility due to their irregular pore structure [9]. Additionally, amines that are grafted onto a catalyst are more vulnerable to leaching in aqueous solutions [10]. Grafting tends to concentrate the groups around the exterior of the particle and tend to form “aminopropyl-

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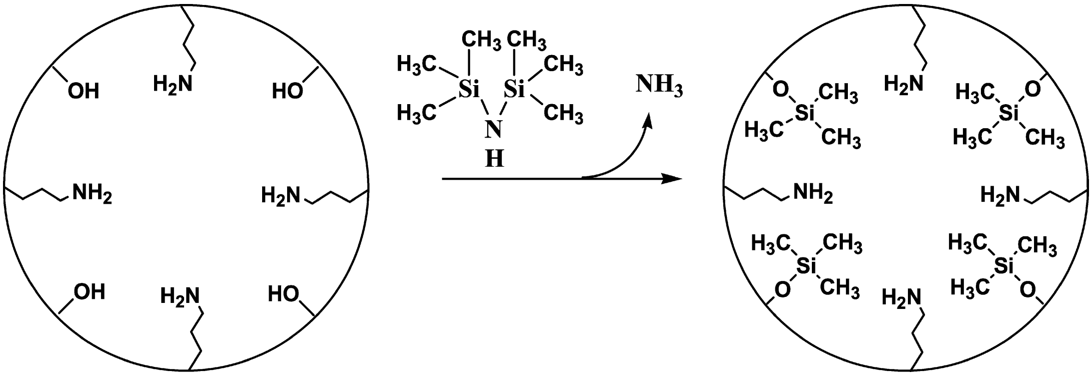

Fig. 1. Silylation reaction of aminopropyl-functionalized SBA-15 by HMDS.

silane islands" [11] while consuming multiple surface hydroxyls per grafted amine [12,13]. Since co-condensation more uniformly incorporates functional silanes into the pore walls more silanols generally remain available for catalytic activity.

Hexamethyldisilazane (HMDS) is commonly used to cap silanols and make silica surfaces hydrophobic. This reagent was used in the present study to observe the effects of the silanols on the catalyst's activity. Chlorosilanes may also be used to silylate silica surfaces, but use of these requires a base catalyst [14,15]. Silylation has been used to avoid inhibition of catalytic activity by surface silanols via hydrogen bonding and formation of zwitterions with primary amines, [16] as well as competitive reactions [17].

The Knoevenagel condensation [18] is a carbon–carbon bond forming reaction commonly used to evaluate both organic [2,3,9,10,19–34] and inorganic [35–44] basic catalysts, so it was used as the probe reaction. This reaction consists of the nucleophilic addition of a methylene group to a carbonyl group, where the methylene group is activated by one or two electron-withdrawing groups. Higher rates of reaction are obtained with aldehydes than with ketones due to steric and electronic effects [28,35].

In the current work, SBA-15 catalysts containing aminopropyl and dihydroimidazole groups were synthesized separately. Portions of each of these synthesized materials were then silylated with HMDS, so that the catalytic activities of all of these materials could be compared to one another as well as to that of a homogeneous base, propylamine.

2. Experimental

2.1. Catalyst synthesis

The aminopropyl-functionalized SBA-15 (APS) and dihydroimidazole-functionalized SBA-15 (DHIS) were synthesized using the co-condensation procedure described by Wang et al. [30,45]. In a typical synthesis, 4 g of the structure-directing agent, Pluronic P123 (BASF Co.) was dissolved in a mixture of 125 ml deionized water and 25 ml hydrochloric acid (12.1 N). Tetraethyl orthosilicate (TEOS) was added as the silica precursor (98%, Acros Organics) at 40 °C. The functional silane, either 3-aminopropyltriethoxysilane (APTES) (99%, Aldrich) or *N*-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (IPTES) (Gelest), was added after a TEOS prehydrolysis period of one hour. The resulting mixture (1 TEOS:0.1 APTES/IPTES:7.76 HCl:171 H_2O molar ratio) was stirred at 40 °C for 20 h and aged at 90 °C for 24 h before being filtered. The surfactant template was removed by refluxing in ethanol with 10 wt% hydrochloric acid for 24 h. The catalyst was then filtered and washed with ethanol. Excess protons from the acidic synthesis conditions were removed with a 5 ml tetramethylammonium hydroxide (TMAH) solution (25 wt% in methanol, Acros Organics) in 45 ml methanol while stirring for 30 min.

2.2. Silylation

Following the TMAH treatment step, surface silanols were capped for a portion of the catalytic materials via silylation using an excess of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (ReagentPlus®, 99.9%, Aldrich) [46]. In order to avoid having traces of water in the pores during silylation, the catalysts were dried under vacuum at 100 °C (20 μm Hg for 5 h). 5 ml of HMDS was diluted in 5 ml toluene before addition to the suspension of the catalyst in toluene in a dry box. The mixture was refluxed for 24 h and was subsequently filtered and washed with toluene and ethanol. Fig. 1 is a schematic of the sequential reaction of one molecule of HMDS with two silanols releasing ammonia and leaving the amine intact.

2.3. Characterization

Nitrogen adsorption/desorption was performed at −196 °C with a Micromeritics ASAP 2020 system to obtain BET specific surface areas and BJH pore size distributions. Thermogravimetric analysis (TGA) of silylated and unmodified aminopropyl-functionalized SBA-15 (APS) and dihydroimidazole-functionalized SBA-15 (DHIS) was performed with a Perkin-Elmer TGA7 for identification and quantification of functional groups using a temperature ramp of 5 °C/min in a high purity nitrogen purge. The weight percent of nitrogen in each catalyst was determined by elemental analysis using a Perkin-Elmer Series II 2400 CHN analyzer. Fourier transform infrared spectroscopy (FTIR) transmission data were collected for pressed catalyst pellets made with potassium bromide using a Nicolet 6700 FT-IR (Thermo Electron Corp.).

2.4. Catalytic testing

Reactants for the Knoevenagel condensation reaction, benzaldehyde (ReagentPlus®, 99+%, Aldrich) and ethyl cyanoacetate (98+%, Aldrich), as well as propylamine (99+%), were used as purchased from Sigma-Aldrich. All reactions were performed in a 50-ml round-bottom flask agitated by magnetic stirring at 25 °C with equimolar amounts of the reactants. The reaction was performed under a nitrogen blanket, which was added to purge the flask of air through one neck using a mineral oil bubbler. The catalyst was dried under vacuum at 100 °C (20 μm Hg for 5 h) prior to use. A typical reaction consisted of 0.14 g catalyst, 40 ml solvent (toluene or other as discussed later), 0.07 ml benzene as an internal standard, 0.91 ml benzaldehyde, and 0.96 ml ethyl cyanoacetate at 25 °C. The reaction was initiated by addition of benzaldehyde to the reaction mixture. Samples were taken by syringe through a septum and analyzed using a Varian gas chromatograph (CP-3800) with a Varian CP7417 column and a flame ionization detector. As the condensation reaction of benzaldehyde with ethyl cyanoacetate is inhibited by the presence of water, the