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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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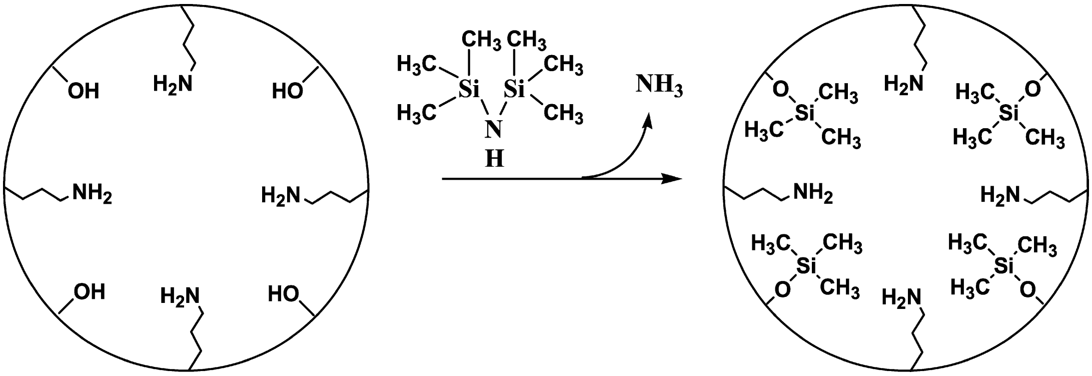

Fig. 1. Silylation reaction of aminopropyl-functionalized SBA-15 by HMDS.

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

Table 1
Nitrogen adsorption/desorption and elemental analysis results for the heterogeneous base catalysts.

	Surface area (m^2/g)	Median pore diameter[a] (Å)	Pore volume (cm^3/g)	N content (mmol/g)
APS	570	52.4	0.75	1.05
Silylated APS	465	50.2	0.60	0.93
SBA-15	680	62.9	1.07	–
Silylated SBA-15	430	60.2	0.74	–
DHIS	610	60.3	0.88	1.01
Silylated DHIS	455	57.0	0.72	0.93

[a] From BJH adsorption.

reactants were diluted in toluene and turnover numbers were calculated at moderate conversions to minimize the concentration of water and, hence, equilibrium effects. The calculated turnover numbers were based on the conversion after 45 min of reaction time.

3. Results and discussion

3.1. Characterization

For the silylated materials, the hydrophobicity of the catalyst was qualitatively apparent in its inability to be dispersed in water. Silylation was also confirmed by TGA, with a weight loss of about 10% of the total catalyst weight at around 400 °C, which was consistent with the literature [47]. As found previously with grafting, a nonpolar solvent allows aggregation of the silylation agent at the catalyst surface thereby favoring interaction with the silanols [48]. Previously, the steric hindrance of the three methyl groups per silanol in HMDS resulted in incomplete surface coverage, which was found to be 82% by Anwander et al. [15]. However, it is believed that the long reaction times allowed for silylation facilitated capping of all of the catalytically accessible silanols.

Nitrogen adsorption–desorption isotherms for the synthesized materials were of type IV with H1 hysteresis, characteristic of mesoporous solids with cylindrical pores [49]. Physical properties of the materials are given in Table 1. The data for the silylated APS indicated a reduction in surface area and a slight reduction in pore size while maintaining the pore structure. The reduction in surface area upon silylation is consistent with previous reports [16,17]. A comparison of the adsorption/desorption isothermals and pore size distributions for the APS and silylated APS samples is shown in Fig. 2. The minor reduction in pore diameter implies that mass transfer within the pores of the unmodified and silylated catalysts should be approximately equal, allowing the direct comparison of reaction data.

FTIR spectra for the APS and silylated APS materials are shown in Fig. 3. Incorporation of trimethylsilyl groups was confirmed by the Si–CH_3 antisymmetric deformation stretch at 1410 cm^{-1} [50]. Both the silylated and unsilylated silicas display a large, broad silanol band in the region of 3700–3200 cm^{-1}. However, the silylated catalysts showed a significant decrease in the silanol bands. This result is mainly due to the conversion of silanols to trimethylsilyl groups, but the decrease is also likely due in part to diminished water adsorption from an increase in hydrophobicity [51]. Free silanols have O–H stretching bands around 3740 cm^{-1}, while hydrogen-bonded silanols display stretching around 3600–3500 cm^{-1} [52]. FTIR cannot distinguish between single and geminal silanols, [52] as a result, peaks for the different silanols form a broad band. A Si–O–H stretching band can also be found in the region of 920–830 cm^{-1} [50]. Large peaks protrude from the broad silanol band around 2970 cm^{-1} in the silylated samples, corresponding to C–H stretching vibrations of the methyl groups [46, 53]. There is also a $SiCH_3$ band at 850 cm^{-1} [50]. The significantly smaller adsorbed water peak around 1630 cm^{-1} reveals the reduction in surface hydrophilicity [50].

3.2. Reaction considerations

Two mechanisms for the base-catalyzed Knoevenagel condensation have been proposed in the literature: a mechanism involving a covalent imine intermediate with the base group [20,26] and an ion-pair mechanism [2,26]. The presence of the imine intermediate for the former has been confirmed by *in situ* attenuated total reflection modulation infrared spectroscopy [26,32]. Inorganic catalysts such as basic zeolites and higher order amines have been proposed to catalyze the reaction by the ion-pair mechanism [40, 54]. The ion-pair mechanism involves base abstraction of a proton from the methylene carbon, forming a carbanion, which attacks the carbonyl carbon, forming an enol. The reaction concludes with elimination of the hydroxyl group, forming a double bond and releasing water [40]. When uncatalyzed, the reaction proceeds through this mechanism in protic solvents [55]. The reaction order of the ion-pair pathway can be either first or second, depending on whether the proton abstraction step or the condensation step is rate-limiting, respectively [41]. The ion-pair mechanism appears to be favored by tertiary amine groups, while primary amines, being weaker bases, favor the imine intermediate [26,40]. As a result of these different mechanisms for different types of bases, the

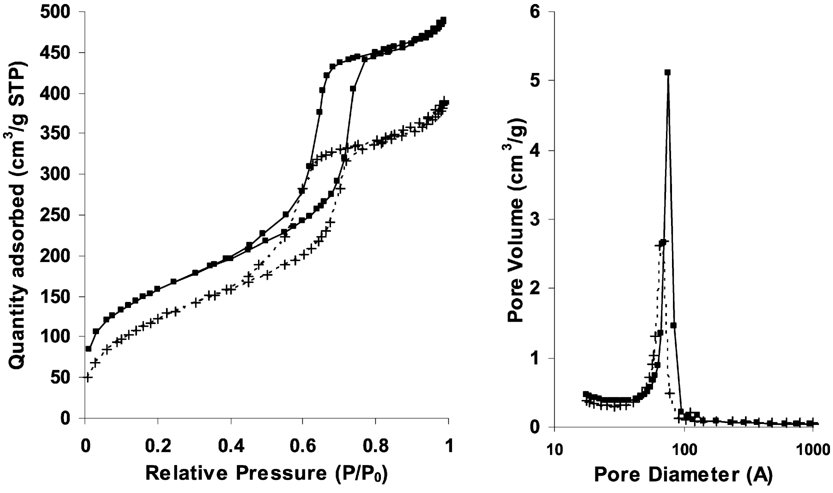

Fig. 2. Nitrogen adsorption/desorption data for unmodified (■) and silylated (+) APS. (Left) Nitrogen adsorption and desorption isotherms. (Right) BJH adsorption pore size distribution.

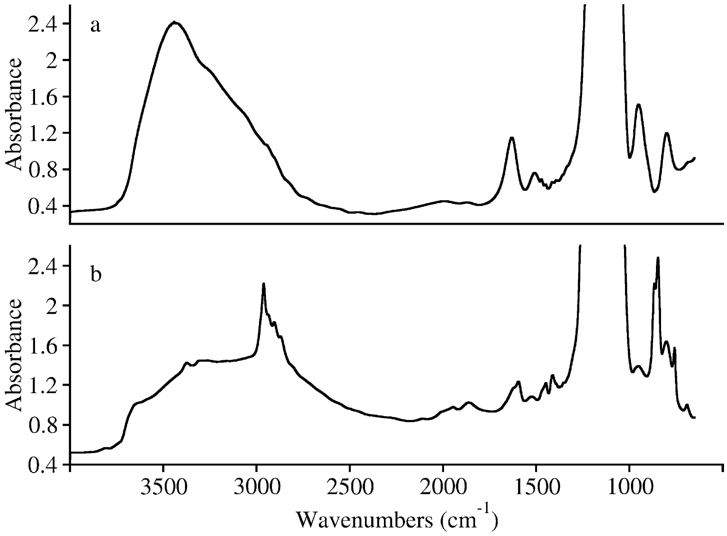

Fig. 3. FTIR spectra of (a) aminopropyl-functionalized silica (APS) and (b) silylated APS.

strength of the Brønsted base does not necessarily correlate with its catalytic activity.

Cooperative effects in the Knoevenagel condensation were first proposed by Hein et al. [56] using a weakly basic ion-exchange resin, Dowex 3, in a mixture with acetic acid. The authors found that the acetate salt of Dowex 3 was more active than the resin alone but less active than the free basic form of the resin mixed with acetic acid. In the authors' proposed mechanism, free acetic acid molecules activated the carbonyl while the basic resin moiety abstracted a proton from the methylene group. An equimolar combination of a weakly acidic (carboxylic acid) ion exchange resin and an aqueous base, $H_2N(CH_2)_2N^+Me_3OH^-$, has also been used as an acid–base catalyst system [57]. The resin alone showed no catalytic activity. Use of a sulfonic acid resin, Amberlyst 15, with an amine was found to be ineffective in the condensation of benzaldehyde with ethyl cyanoacetate at room temperature due to the higher strength of the acidic moiety. The homogeneous equivalent of the amine and *n*-caproic acid also had little catalytic activity [57]. Another cooperative interaction for the Knoevenagel condensation was reported by Kubota et al. [58], who found higher catalytic activities for organic cationic-MCM-41 composites than for the organic cations free in solution.

Acid–base bifunctional catalysis in the Knoevenagel condensation has been reported for inorganic catalysts via the ion-pair mechanism by Ebitani et al. [39] using reconstructed hydrotalcite. The proposed mechanism began with the Al^{3+} cation acting as a Lewis acid site, coordinating with the nitrile group, thereby facilitating abstraction of the ethyl cyanoacetate proton and thereby stabilizing the resultant carbanion. Mild acid–base pairs in amorphous aluminophosphates and zirconophosphate oxynitrides have shown similar results, where acid–base pairs are more active than solitary bases of greater strength [37,42].

Angeletti et al. proposed adding participation of a neighboring silanol to the ion-pair mechanism in which the silanol forms a hydrogen bond with an aromatic aldehyde, thereby promoting nucleophilic addition of the anionic methylene compound [19]. The participation of silanols in the reaction is also suggested by results of an infrared study by Corma et al. [23], where benzaldehyde was physisorbed onto substrates with different silanol densities, silica gel and MCM-41, with grafted “proton sponges,” 1,8-bis(dimethylaminonaphthalene). The authors found that the concentration of activated benzaldehyde was higher on MCM-41 than on silica gel, since the silica gel contained fewer silanol groups. This increase in activated benzaldehyde was found to correspond to higher catalytic activity in that study. However, it is possible that the role of the silanol in the condensation reaction is not merely hydrogen-bonding, but possibly transferring a proton. Such a role has been proposed in the literature for another cooperative system, a Henry reaction catalyzed by aminopropyl-functionalized silica gel [2]. If this silanol proton transfer were also the case for the Knoevenagel condensation using the base-functionalized mesoporous silica described here, one could speculate the steps of a cooperative mechanism, as shown in Fig. 4.

Similarly, cooperation between primary amine groups and silanols can also potentially aid in the formation of an imine intermediate. This possibility is suggested in a study by Hine et al., who demonstrated intra-molecular acid catalysis of the formation of imines from acetone and amines with hydroxyl groups [59]. That study highlighted the ability of a hydroxyl group to protonate an amine in a bifunctional manner. A range of acid strengths have been reported for silanols, depending on the type of silanol and with some variation between studies, but these studies confirm that the pK_a values of the silanols are below those of the bases used here, indicating their suitability for proton transfer [60–62]. More recently, Bass et al. proposed a cooperative acid–base mechanism for the imine intermediate pathway of a Henry reaction in their aminopropyl-functionalized silica gel [2]. Correspondingly, the postulated steps of an acid–base cooperative mechanism for the Knoevenagel condensation reaction with a primary amine group are shown in Fig. 5 [2].

3.3. Catalytic testing

Shown in Table 2 are the Knoevenagel condensation reaction turnover numbers for the different catalysts systems performed at 25 °C to minimize mass transfer effects. The turnover numbers were based on the number of sites per gram of catalyst as determined by elemental analysis. The aminopropyl-functionalized SBA-15 (APS) and dihydroimidazole-functionalized SBA-15 (DHIS) catalysts were active for the condensation reaction, with turnover numbers of 15.52 and 18.72 mol/site/h, respectively, whereas the homogeneous propylamine showed little activity, with a turnover number of 0.66 mol/site/h. Silylation of both catalysts resulted in a significant loss of activity, falling to 1.52 mol/site/h for APS and 3.46 mol/site/h for DHIS. The only minor reduction in pore diameter shown in the nitrogen adsorption/desorption results suggested that the rate suppression rate for the silylated APS for the condensation reaction was due to the lack of surface silanols rather than

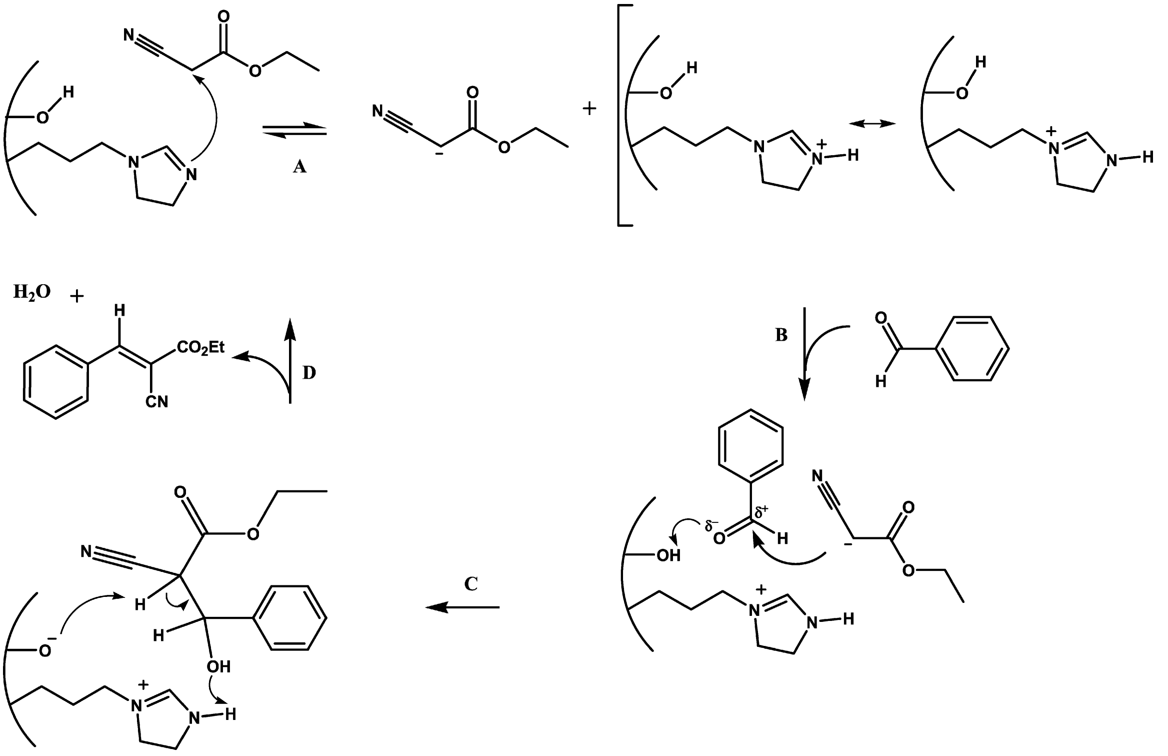

Fig. 4. Postulated steps of the cooperative ion-pair mechanism. (A) The basic nitrogen abstracts a methylene proton, generating a carbanion. (B) The silanol protonates the benzaldehyde oxygen. (C) The carbanion reacts with the activated benzaldehyde. (D) Water and ethyl cyanocinnamate are formed and the catalyst returns to its initial state.

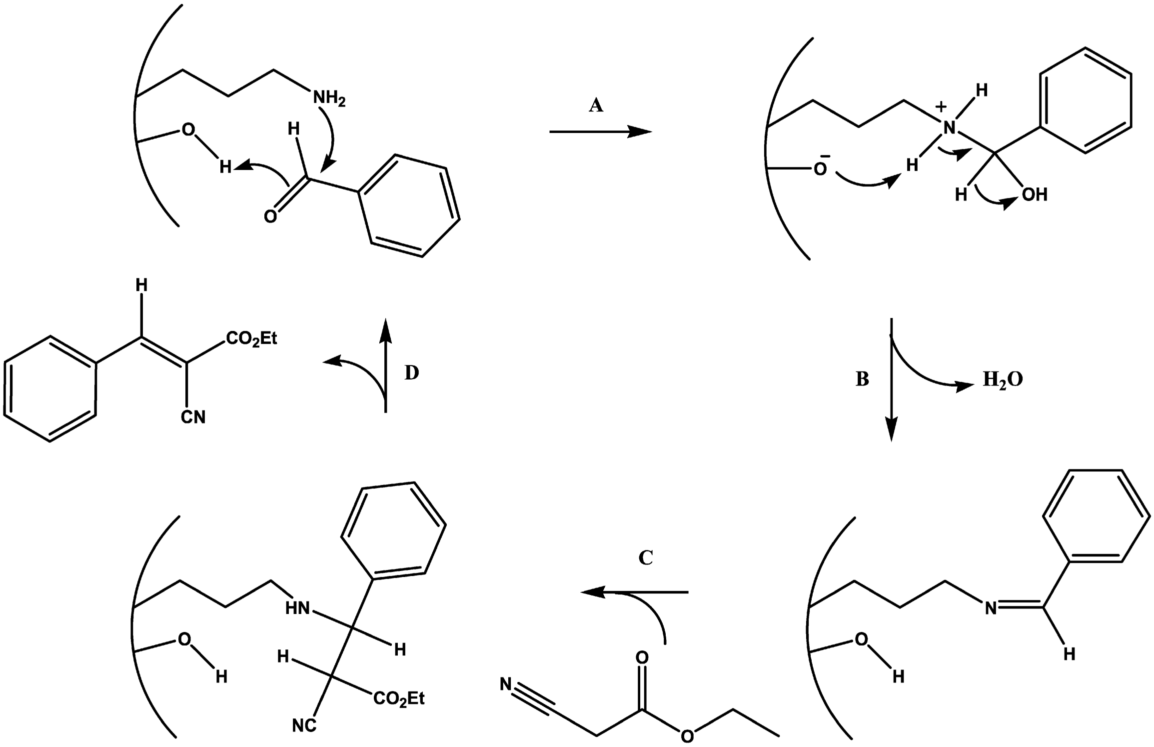

Fig. 5. Postulated steps of the cooperative primary amine mechanism [2]. (A) The silanol protonates the benzaldehyde oxygen while the amine undergoes nucleophilic attack on the carbonyl carbon. (B) Water is released in the formation of imine intermediate. (C) Ethyl cyanoacetate reacts with the intermediate. (D) Ethyl cyanocinnamate is formed and the amine is regenerated.

resistance to internal mass transfer or blockage of amine sites. The silylated APS material turnover number was still greater than that for the homogeneous propylamine. It is interesting to note that the difference in activity between the APS and silylated APS is similar to that reported in the work by Bass et al. [3].

To determine whether the reaction needed silanol groups located in close proximity to the basic site, the activity of free propylamine in the presence of either unfunctionalized SBA-15 or silylated SBA-15 with co-condensed aminopropyl groups was tested. The conversion results for these tests are shown in Fig. 6.

Table 2
Knoevenagel condensation turnover numbers for homogeneous and heterogeneous base catalysts at 25 °C.

	Solvent	Turnover number (mol/site/h)
APS	Toluene	15.52 ± 1.24
Silylated APS	Toluene	1.52 ± 0.97
Propylamine	Toluene	0.66 ± 0.20
Propylamine + SBA-15	Toluene	3.78 ± 1.02
Propylamine + silylated SBA-15	Toluene	0.78 ± 0.26
DHIS	Toluene	18.72 ± 0.79
Silylated DHIS	Toluene	3.46 ± 0.92
DHIS	Acetonitrile	7.35 ± 0.81
Silylated DHIS	Acetonitrile	3.28 ± 0.36
DHIS	Methanol	22.39 ± 0.63
Silylated DHIS	Methanol	15.83 ± 0.79

Reaction conditions: 25 °C, 40 ml toluene. Errors represent 95% confidence intervals.

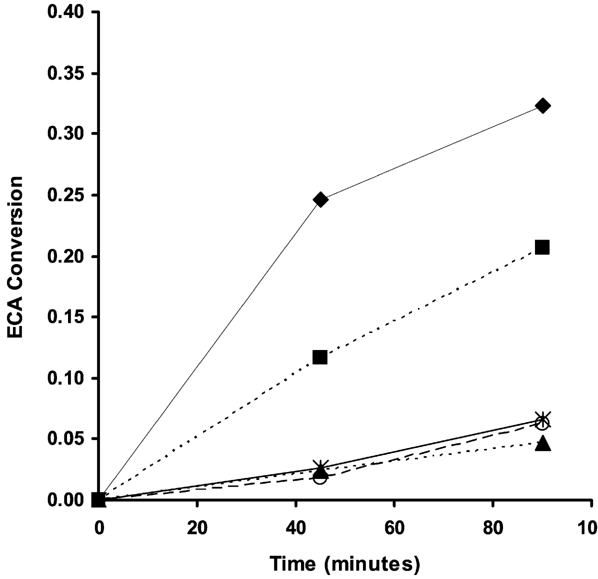

Fig. 6. Conversion of ethyl cyanoacetate in toluene at 25 °C. (○) Homogeneous propylamine, (◆) aminopropyl-functionalized SBA-15 (APS), (■) mixture of propylamine and unfunctionalized SBA-15, (∗) silylated APS, (▲) mixture of propylamine and silylated, unfunctionalized SBA-15.

Interestingly, the combination of unfunctionalized SBA-15 silica with free propylamine resulted in higher conversion than with the free propylamine alone, 21% versus 6% at 90 min, although the combination did give lower conversion than the co-condensed aminopropyl-functionalized silica, 32% at 90 min. It is possible that propylamine may form the imine intermediate while free in solution before diffusing near the silanols. As demonstrated by the comparative rates, the location of the tethered basic site in close proximity to silanols gave a significantly higher rate of reaction. This behavior has also been reported in the literature by Kubota et al., who demonstrated higher catalytic activities for FSM-16-supported secondary amines than those for homogeneous secondary amines mixed with FSM-16 in an aldol reaction [63].

The dihydroimidazole-functionalized silica is a stronger base than the primary amine-functionalized silica, but is unable to form the imine intermediate and must proceed through the carbanion intermediate. The reaction rate for this amine was also aided by having surface silanols in close proximity as shown by the conversion results in Fig. 7, where silylation decreased the conversion at 90 min from 36% to 7%. This catalyst, with a moiety that is a stronger base than propylamine, displayed slightly higher activity than the APS catalyst. Despite having different underlying mechanisms, silylation of the DHIS catalyst had similar results to that of the APS catalyst, showing a significant reduction in activity. Silylation of the DHIS possibly reduces activity in two ways: a loss of silanols to act as cooperative acids as well as a loss of stabilization of the carbanion intermediate in a nonpolar environment.

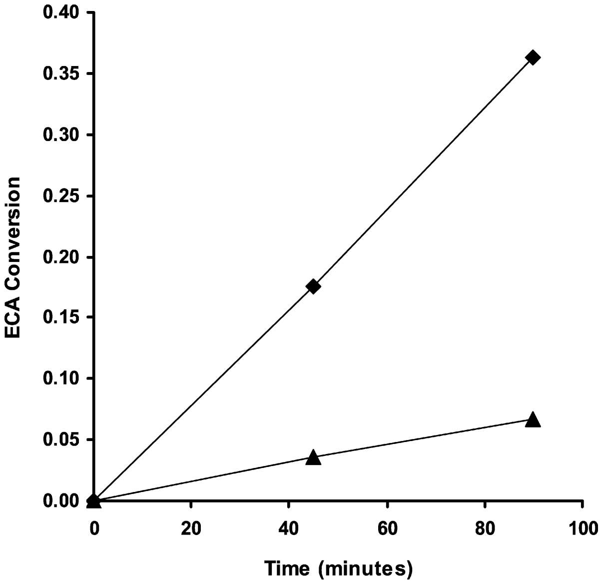

Fig. 7. Conversion of ethyl cyanoacetate at 25 °C in toluene with (◆) dihydroimidazole-functionalized SBA-15 (DHIS), (■) silylated DHIS.

Comparison of the conversion results provided some additional information about the reaction system. Unfunctionalized SBA-15 alone displayed no catalytic activity, which was consistent with the literature [64]. A mixture of silylated APS particles with unmodified SBA-15 silica particles showed approximately the same catalytic activity as the silylated APS, demonstrating that the silanols and amine moieties must be in proximity in order to attain significantly higher reaction rates. Additionally, this result indicates that the contribution from the silica support was due to the participation of the silanols rather than the adsorption of water onto the silica surface, which would remove water produced by the condensation reaction from solution. Incomplete silylation of the silanols could account for the slight increase in turnover number for the propylamine in solution with silylated SBA-15 over the free propylamine alone. Previous studies have shown that the steric bulk of the three methyl groups as well as hydrogen-bonding of silanols prevents complete silylation by HMDS [15,65,66]. However, it is likely that HMDS reacted with nearly all of the accessible, reactive silanols. Another possible explanation is that, although much care was taken to wash the catalyst after silylation and to dry the catalyst using heat and strong vacuum, there could have been some traces of ammonia left adsorbed on the surface of the catalyst that could have contributed to the reaction rate. The nearly identical activities of the homogeneous propylamine and the propylamine in solution with silylated, unfunctionalized SBA-15 indicate that this is likely to be minor.

3.3.1. *Apparent activation energies*

Apparent activation energies were calculated from initial rates data obtained at 25, 35 and 45 °C in toluene (the boiling point of propylamine is 48 °C [67]). Using an overall second-order rate law that was first-order with respect to ethyl cyanoacetate and benzaldehyde, which had a linear fit with an R^2 value greater than 0.99, apparent activation energies of 25.3 kJ/mol for the homogeneous propylamine and 61.2 kJ/mol for the APS catalyst were determined. Calculating apparent activation energies using a first-order (ethyl cyanoacetate only) rate law resulted in a slightly poorer fit but similar numbers, similar to a study with the same reactants but different catalysts, alkaline-substituted sepiolites [41].

Pre-exponential factors of 0.42 and 18 L/mol/s were calculated for the homogeneous and heterogeneous catalysts, respectively. The result for the combination of unfunctionalized SBA-15 and homogeneous propylamine gave an intermediate value of 32.1 kJ/mol with a pre-exponential factor of 5.1 L/mol/s. Interestingly, the more active heterogeneous catalyst was found to have a higher activation energy than the less effective homogeneous catalyst.

Reports of activation energies in the literature for the same reactants indicate that the values found in the current work are consistent. For homogeneous catalysts operating via the ion-pair mechanism, activation energies for the condensation of benzaldehyde and ethyl cyanoacetate reported in the literature range from 21 to 37 kJ/mol (5 to 8.8 kcal/mol) [22,29]. Whereas, for some alkaline-substituted sepiolites (Li, Na, K, Cs on magnesium silicate), which also form the carbanion intermediate, activation energies from 32 to 72 kJ/mol have been reported for the same reactants in the absence of a solvent [41]. That study was a continuation of work using zeolites as the support for the same alkali metal cations in which the authors compared the activity of their heterogeneous catalyst to homogeneous pyridine [40]. Pyridine was found to have an intermediate activity between X and Y zeolites, where X zeolites are more basic and more active, as well having an intermediate activation energy of 44.3 kJ/mol. Interestingly, pyridine was less active than all but one of the sepiolite catalysts, yet its activation energy was lower than those for the lithium and sodium catalysts and higher than those for the potassium and cesium catalysts.

The trend in the pre-exponential factors appeared reasonable, since the reactants encountering amine sites incorporated in the mesoporous silica would also be in proximity to one or more silanols, making the site better positioned for catalysis than the homogeneous amine by itself. When dispersed with unfunctionalized silica, the homogeneous amine could diffuse through the solvent and interact with reactants at the silica surface. Since the amine groups in this case were not fixed to the surface, a lower probability of successful alignment of the reactants with the catalyst would be expected.

3.3.2. *Solvent effects*

To better discern the effects of silylation on catalytic activity, the DHIS and silylated DHIS catalysts were also tested using either methanol or acetonitrile as the solvent. These experiments were necessary because silylation turns a hydrophilic silica surface into a hydrophobic surface, which would affect the interactions between the reagents and the catalytic sites. The difference between the imine intermediate and ion-pair mechanisms was apparent in opposing solvent trends reported in the literature. Activity of catalysts using the ion-pair mechanism increased in solvents with increasing polarity, while the opposite was true for heterogeneous primary amine catalysts [21,23,27,43]. Nonpolar solvents appeared to aid the primary amine mechanism by concentrating the reactants at the catalyst surface [21]. Al-Haq et al. [33] demonstrated an opposite trend with aminoalkyl modified polysilsesquioxanes, where catalytic activity increased with increasing solvent polarity. These results appeared to support the hypothesized partitioning effect since the polysilsesquioxanes are more hydrophobic than silica materials synthesized using tetraethoxysilane or tetramethoxysilane, and consequently, would not concentrate polar reactants near the catalyst surface. This suggests that the activity of the combination of unfunctionalized SBA-15 and homogeneous propylamine may be aided in part by some partitioning of the propylamine near the hydrophilic surface. Polar solvents aid the ion-pair mechanism by stabilizing the carbanion intermediate, as shown by observed activation energies in various solvents by Rodriguez and Corma et al. [29] using an unsupported organic "proton sponge" catalyst. This study reported activation energies of 5 kcal/mol when dimethyl sulfoxide was the solvent, 8.5 kcal/mol for chlorobenzene and 7–7.3 kcal/mol for no solvent. Corma et al. [23] found that having sufficient silanols on the silica surface appeared to stabilize the transition state, thereby reducing the effect of the solvent on catalytic activity. Despite the inhibition of condensation reactions by water, the Knoevenagel condensation reaction was shown to proceed in aqueous solution presumably due to stabilization of the ion-pair intermediate [24].

The activity results for the DHIS functionalized silica catalysts in different solvents are shown in Table 2. When acetonitrile (dielectric constant, $\varepsilon_r = 37.5$ [67]) was used as the solvent, the condensation reaction catalyzed by DHIS was significantly slower than that obtained in either toluene or methanol probably due to the solvent's inability to stabilize the carbanionic intermediate [67]. The activity of the silylated catalyst was slightly lower in acetonitrile than in toluene. This indicates that the polar capping agent used by Bass et al., dimethyl cyanopropyl chlorosilane, is not ideal for a study of this catalyst system and highlights the need for catalytic testing in a solvent that can stabilize the intermediate in order to distinguish between noncovalent interactions and acid–base cooperativity [2].

The condensation of ethyl cyanoacetate and benzaldehyde in methanol ($\varepsilon_r = 32.6$ [67]) was complicated by base-catalyzed transesterification of ethyl cyanoacetate and ethyl cyanocinnamate into methyl cyanoacetate and methyl cyanocinnamate, respectively [38]. Interestingly, the transesterification reaction in methanol without benzaldehyde was negligible when the silylated DHIS catalyst was used. However, despite the added complexity of the transesterification side reaction with methanol as the solvent, conclusions may still be drawn from the conversion of benzaldehyde as well as from the combined conversion of the two alkyl cyanoacetates even in the presence of methanol. The catalyst displayed higher activity in methanol than in toluene, which is consistent with other organic catalytic groups supported on silica that operate via the ion-pair mechanism [23]. Although there was a slight decrease in activity for silylated DHIS, the effect of silylation was not nearly as dramatic in methanol as that seen in toluene. As the influence of solvent on activity became less significant when polar, protic solvents were used, as shown in the literature [23]. Similarly, that current results show that methanol, a protic solvent, appears to stabilize the carbanion intermediate, thereby reducing the effect of the silanols. It is important to note that this observation does not conflict with the proposition of the silanol acting cooperatively as an acid in the Knoevenagel condensation reaction. The activity difference between the DHIS and silylated DHIS catalysts in general was much greater than the activity difference between the DHIS catalyst in toluene and in methanol. This result supports that hypothesis the silanols do not merely hydrogen bond with the reactants. Additionally, the small decrease in activity of the silylated DHIS in methanol and the relative ease of the transesterification reaction indicated that the large decrease in activity with toluene as the solvent was not due to mass transfer effects or steric hindrance of the trimethylsilyl groups.

4. Conclusions

Random incorporation of amines via co-condensation of SBA-15 was found to yield acid–base cooperative catalysis with surface silanol groups. While cooperative activity was achieved with a solution containing a mixture of propylamine and SBA-15, the activity increased significantly when the aminopropyl groups were attached near silanol groups. Thus, previous single-site results can in some cases be extended to a more extended catalytic domain where the active sites are not rigorously isolated as in functionalized mesoporous silica. Additionally, this study has shown that the dihydroimidazole moiety, which catalyzes the Knoevenagel condensation via an ion-pair mechanism, also displays acid–base cooperative behavior. While solvent effects were significant, the presence of silanols was shown to have a greater impact on catalytic activity. These results support the hypothesis that the silanols act as acids rather than merely stabilizing transition states with hydrogen bonds. While solvent effects were significant, the presence of silanols was shown to have a greater impact on catalytic activity. Consideration of these results can be of use when designing a co-condensed acid–base bifunctional catalyst, where the proximity of the acid and base groups determines catalytic activity and reaction selectivity. Additionally, the silylation experiments performed here may also be of use when testing a new acid–base catalyst in order to elucidate the catalytic mechanism of the organic moiety from the effects of silanol groups.

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Supplementary material

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