

Tuning Cooperativity by Controlling the Linker Length of Silica-Supported Amines in Catalysis and CO₂ Capture

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S Supporting Information

ABSTRACT: Cooperative interactions between aminoalkylsilanes and silanols on a silica surface can be controlled by varying the length of the alkyl linker attaching the amine to the silica surface from C1 (methyl) to C5 (pentyl). The linker length strongly affects the catalytic cooperativity of amines and silanols in aldol condensations as well as the adsorptive cooperativity for CO₂ capture. The catalytic cooperativity increases with the linker length up to propyl (C3), with longer, more flexible linkers (up to C5) providing no additional benefit or hindrance. Short linkers (C1 and C2) limit the beneficial amine–silanol cooperativity in aldol condensations, resulting in lower catalytic rates than with the C3+ linkers. For the same materials, the adsorptive cooperativity exhibits similar trends for CO₂ capture efficiency.

Tuning cooperative interactions between two identical or different sites has important implications for many systems, including ligand–receptor binding,¹ catalysis,^{2–5} and CO₂ adsorption.^{6–8} The ultimate examples of tuned cooperative interactions involve protease enzymes that typically employ a trio of catalytic sites (the catalytic triad⁹), including acidic, basic, and hydrogen-bonding residues. These highly evolved sites have complex architectures that facilitate the precise organization of acid and base groups to activate both the reacting electrophile and nucleophile in catalytic reactions. The complex enzyme architecture spatially organizes the functional groups and maintains a degree of flexibility that allows the catalytic sites and substrates to adopt a favorable conformation to promote the cooperative interaction. Slight modifications of these parameters can have a significant impact on the catalytic rates and even the mechanistic pathways.^{2,10,11}

Some of these enzyme features can be achieved in simpler catalysts through the synthesis of bifunctional molecules^{11–15} and/or via immobilization of the acid and base components on a support in such a way that quenching is not possible because of the restricted mobility or weak interactions of the sites.^{16–19} Past works have colocalized the acid and base sites on organic molecules such as amino acids¹⁴ and ionic liquids²⁰ or on polymeric¹⁸ or mesoporous silica supports.²¹ Of particular importance is the acid–base cooperative catalytic interaction of amines and silanols that was first demonstrated for a soluble amine mixed with mesoporous silica.²² The benefit of acid–base colocalization on solid supports was subsequently demonstrated through immobilization of primary amines on mesoporous silica at moderate densities.^{21,23} Trimethylsilyl

capping of the silanols eliminated the beneficial acid component and decreased the observed rate of reaction, confirming the importance of the cooperative interactions, but significantly modifying the local environment. Subsequent studies using primary amines have focused on tuning the strength of the acid site.^{17,24,25} A consensus is forming that weaker acid sites result in the greatest enhancement of the reaction rate in prototypically base-catalyzed coupling reactions such as the aldol condensation, with many examples utilizing surface silanols as the weak acid component.^{21,23,26,27} While the importance of tuning the acid strength has been demonstrated, no studies have investigated the impact of the length and flexibility of otherwise electronically similar amines in their cooperative interactions with the silanols.

Amine–silanol interactions have also recently been suggested to be important in the adsorption of CO₂.²⁸ Surfaces grafted sparsely with propylamines so they could easily interact with silanols effectively adsorbed carbon dioxide. Capping the silanols decreased the carbon dioxide adsorption. While this trend was unambiguous, it is unclear whether the cause was associated with prevention of cooperative amine–silanol interactions or simply isolation of the amine sites as a result of the introduction of the bulky trimethylsilyl groups. The latter issue, isolation, is important because two amines are typically thought to be required to adsorb CO₂ under dry conditions, resulting in a maximum amine efficiency^{29,30} of 50% (i.e., 0.5 mol of CO₂ adsorbed/mol of amine). With the cooperative amine–silanol mechanism, an amine efficiency of 100% is theoretically possible provided that the amines have sufficient flexibility to interact with adjacent silanols. Since the organosilane is relatively expensive, a higher amine efficiency would be very desirable from a practical perspective.

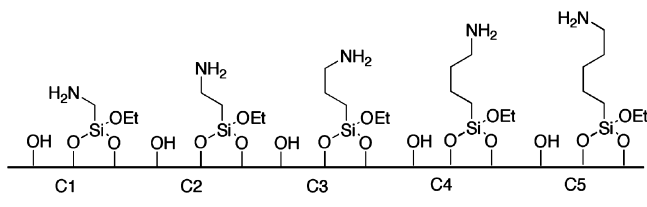
In this work, the effect of the spatial separation of the amines and silanols was investigated by systematically varying the alkyl chain length of the organosilane grafted onto a well-defined SBA-15 mesoporous silica support. Using an array of materials functionalized with alkyl linkers varying from methyl to pentyl (Scheme 1), we determined the amine linker length dependence of the reaction rate for the acid–base cooperative aldol condensation of 4-nitrobenzaldehyde and acetone. The importance of amine–silanol interactions during CO₂ adsorption was also demonstrated, and structure–function trends for the two applications have been elucidated.

A description of the synthetic procedures for organosilane synthesis, surface grafting, material characterization, catalytic

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Scheme 1. Aminosilanes Grafted onto Mesoporous SBA-15 Silica with Controlled Linker Lengths, Including C1 (Methyl), C2 (Ethyl), C3 (Propyl), C4 (Butyl), and C5 (Pentyl)



testing, and CO₂ adsorption testing can be found in the Supporting Information (SI), but a brief summary is provided here. Only two of the five organosilanes used were available commercially. The other three aminosilanes were synthesized from the appropriate halogenated alkylsilanes using anhydrous ammonia in a Parr reactor.³¹ The pentyl-based organosilane required an initial hydrosilylation of 5-bromo-1-pentene with triethoxysilane to yield the alkylsilane.³² NMR characterization confirmed the syntheses of the three relatively uncommon organosilanes.

The different organosilanes were separately grafted onto calcined SBA-15 silica under mild conditions. Extensive characterization using standard techniques, including ¹³C cross-polarization magic-angle-spinning (CP-MAS) NMR spectroscopy, elemental analysis, and nitrogen physisorption, confirmed the functionalization (Figures S1–S10 in the SI). All of the materials were functionalized with low molar loadings that were approximately equal (~0.32 mmol g^{−1}) based on nitrogen content from elemental analysis. Still, slight differences in the grafting density due to differences in the hydrophobicities, reactivities, and polarities of the organosilanes could be expected. The low loadings allowed efficient acid–base (silanol–amine) catalytic cooperativity and permitted direct investigation of the effect of the linker length on the chemical reactivity.

The materials were tested for pseudo-equilibrium CO₂ adsorption capacity using 400 ppm CO₂ in He to limit the amount of physisorbed CO₂, thereby probing the behavior of the amine sites. The moisture-free conditions used to measure CO₂ capacity meant that CO₂ was adsorbed in one of two manners: (1) adsorption utilizing two primary amine groups or (2) adsorption between an amine and silanols on the surface, as observed by Weitz and co-workers using differential FTIR measurements with 2% CO₂.²⁸ The relative importance of these two mechanisms depends on the amine density. In view of the low amine loadings used, the latter mechanism was surmised to be more important.

The amine efficiencies for all of the materials are shown in Figure 1 (numerical values are given in Table S1 in the SI). The material with the shortest linker (C1) adsorbed a very small amount of CO₂ (0.024 mmol g^{−1}), resulting in an amine adsorption efficiency of only 8%. The low amount of adsorption was less than that by the bare support material (i.e., 0.032 mmol g^{−1}), indicating that the organosilane does not significantly contribute to the adsorption of CO₂ and additionally blocks potential CO₂ physisorption sites. The low amine efficiency indicates that the low flexibility of the amine site limits the interaction of the amine with the surface and that the amine sites are relatively isolated from one another. Further flexibility was imparted to the amine group by using the ethyl linker (C2), yet only a slight increase in amine

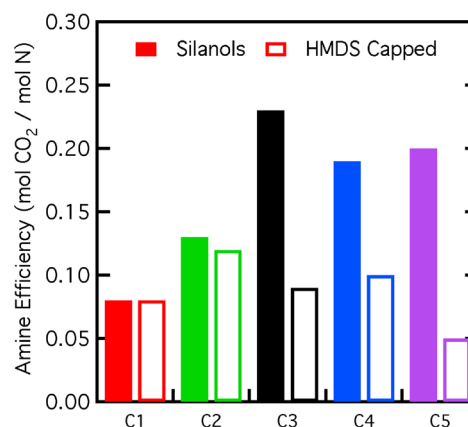


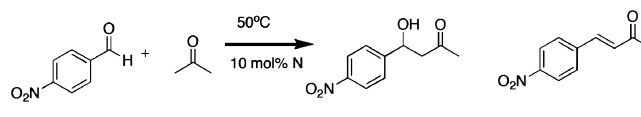
Figure 1. Computed amine efficiencies for adsorption of CO₂ (400 ppm in He) on materials functionalized with amines having different linker lengths.

efficiency to 13% was observed. Adding a third methylene group to the chain provided the necessary flexibility to produce a significant increase in the amine efficiency to ~20%, which is similar to those for highly functionalized materials reported previously in ultradilute CO₂ capture, where amine–silanol cooperativity would not be observed.³³ No further increase in the amine efficiency was observed with the additional flexibility imparted with the butyl or pentyl linkers. If cooperation of amines with silanols were the dominant CO₂ capture mechanism, an increase in amine efficiency might be expected with an increase in linker length, as more amines would be able to interact with silanols. The low amine efficiency suggests that the dominant mechanism of CO₂ adsorption is cooperative amine–amine adsorption, but additional detailed spectroscopic studies are needed to confirm or refute this hypothesis.

The silanols were removed by treating the materials with hexamethyldisilazane (HMDS) to create a second set of materials that were identical to the first except that the vast majority of the surface silanols were removed. Without the silanols, the CO₂ adsorption capacity decreased significantly for materials with the longer linkers (C3 to C5) because the capping molecule disrupted the cooperative interaction necessary for efficient CO₂ adsorption, resulting in amine efficiencies of ~10%.

The materials were also tested for their catalytic efficiency in the aldol condensation of 4-nitrobenzaldehyde with acetone (Scheme 2), a standard test reaction used to assess

Scheme 2. Aldol Condensation of 4-Nitrobenzaldehyde and Acetone



cooperativity in aminosilica materials.^{14,19,34–36} The linker length had a significant impact on the observed reaction rates, as shown in Figure 2. The observed rate increased with the number of carbons in the carbon chain up to the propyl chain. Increasing the linker length beyond propyl resulted in identical catalytic rates. This is in contrast to the results of previous work with carboxylic acids and primary amines, where the additional flexibility associated with longer chains between the functional groups resulted in decreased activity.^{34,37} This observation

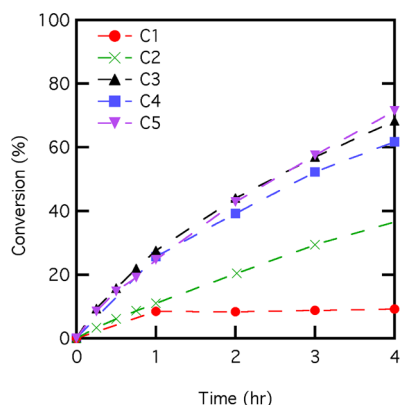


Figure 2. Conversion of 4-nitrobenzaldehyde in the aldol condensation with acetone for the catalysts with different alkyl linkers at 50 °C using a catalyst loading of 10 mol % amine based on CHN analysis.

suggests that the amines and silanols interact only weakly (most likely because of the weak acidity of the silanol), whereas amines and carboxylic acids interact more strongly unless the relative interaction of the two functional groups is constrained, as is the case with proline.¹¹

The material with the shortest chain (C1) had the lowest observed reaction rate. The observed reaction rate with this catalyst showed an interesting behavior. An initial high apparent rate of conversion of 4-nitrobenzaldehyde was observed over the first hour of reaction, after which slow yet gradual conversion occurred over the remaining reaction time. The initial 10% conversion of 4-nitrobenzaldehyde corresponds to the amine loading in the reaction, suggesting a relatively rapid reaction of the aldehyde with the amine sites on the silica surface (Scheme S1 in the SI). We surmise that the adsorbed reactant was not readily converted to the aldol product because the reacted benzaldehyde did not contain a hydrogen α to the carbonyl, preventing the aldehyde from forming the enamine necessary for the reaction to proceed efficiently.³⁸ This demonstrates that the single methylene linker does not permit sufficient flexibility of the amine site to allow the reaction to proceed through a silanol-activated pathway. Instead, the reaction proceeds through a much slower base-catalyzed mechanism at a rate consistent with catalysis by a homogeneous, unsupported primary amine (Figure S11).

The material with a slightly longer chain length (C2) was found to catalyze the aldol condensation with an efficiency between those of methyl (slow) and propyl (fast) functionalized materials. The two most plausible explanations for this observation are that (1) only limited numbers of surface silanols are accessible to the short C2 linkers or (2) the mechanism is modified. The intermediate value of the rate could reflect an irregular placement of the silanols on the silica surface, with some amine sites being within the optimal distance of silanols to enhance the activity and others not. An alternative explanation is that the ethyl linker causes the reaction to proceed through a modified mechanism (see Schemes S2 and S3). Examination of the proposed cooperative mechanism for a proline catalyst showed that the reaction is accelerated at two instances as a result of acidic protonation of a carbonyl, one for the ketone and the other for the aldehyde.^{14,38} The close proximity of the amine and carboxylic acid in proline allows both steps to be cooperatively catalyzed. With the constrained flexibility due to the ethyl linker, the first activation

(acidic activation of the ketone) may not occur to an appreciable extent, whereas the acidic activation of the aldehyde may proceed more readily, resulting in a rate that is faster than that found for the methyl linker but slower than the catalytic rate for the propyl (and longer) linkers. Distinguishing between these two (and other possible) explanations will require additional experimentation.

The acid–base catalytic cooperativity was further confirmed with the silanol-capped materials. The catalytic rates decreased considerably when the acidic silanols were removed, as shown in Figure 3. After silanol removal, the materials with propyl

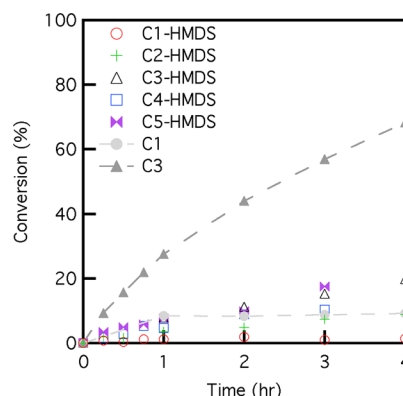


Figure 3. Conversion of 4-nitrobenzaldehyde in the aldol condensation with acetone for the catalysts with different alkyl linkers after HMDS treatment at 50 °C using a catalyst loading of 10 mol % amine based on CHN analysis. The data for C1 and C3 without HMDS treatment are included for comparison.

through pentyl linkers had activities comparable to that of the unmodified methyl-functionalized material, confirming the important role of acid–base cooperativity for the C3–C5 linkers. This further demonstrates that the unmodified aminomethyl group was spatially constrained and unable to catalyze the reaction in a cooperative manner. The methyl- and ethyl-functionalized materials after HMDS treatment gave even lower activities than the propyl material treated with HMDS. The bulky trimethylsilyl groups presumably add steric constraints that further slow the reaction.

The importance of the length of the aminosilane linker in two cooperative chemical reactions, catalysis of the aldol condensation and CO₂ adsorption, has been demonstrated using a systematic array of amine-functionalized silica materials with different linker lengths. Short linkers limited the interaction and correspondingly the amine–silanol cooperativity in catalytic and CO₂ adsorption applications. For the longer linkers (C3–C5), the catalytic and adsorptive cooperativities remained relatively constant, suggesting that amine–silanol quenching reactions do not occur and that a propyl linker is sufficiently long to allow for effective cooperative interactions. These materials should prove highly valuable in further fundamental studies probing the cooperative catalytic mechanisms of other acid–base bifunctional reactions as well as in helping to create more efficient catalysts and adsorbents. In particular, the methyl linker can be used to distinguish between cooperative effects with the surface and outer-sphere effects, as the short linker does not require modification of the surface to limit cooperative surface interactions.²¹

■ ASSOCIATED CONTENT

■ Supporting Information

Syntheses of organosilanes and mesoporous materials; mechanistic proposals for catalytic reactions; and materials characterization, including ^{13}C CP MAS NMR spectra, nitrogen physisorption isotherms, thermogravimetric analysis curves, and X-ray diffraction patterns. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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