Synthesis and Characterization of Bifunctional Surfaces with Tunable Functional Group Pairs

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ABSTRACT

Grafting of pairs of functional groups onto a silica surface was demonstrated by tethering both terminals of an organochlorosilane precursor molecule, $\text{Cl}_2(\text{CH}_3)\text{Si}(\text{CH}_2)_4(\text{CO})(\text{OSi}(\text{i-Pr})_2)(\text{CH}_2)_2\text{Si}(\text{CH}_3)\text{Cl}_2$, that possess a cleavable silyl ester bond, onto a silica surface. Hydrolytic cleavage of the silyl ester bond of the grafted molecule resulted in the generation of organized pairs of carboxylic acid and organosilanol groups. This organosilanol moiety was easily transformed into other functional groups through condensation reactions to form, together with the neighboring acid group, pairs such as carboxylic acid/secondary amine, carboxylic acid/pyridine, and carboxylic acid/phosphine. In the case of carboxylic acid/amine pairing, there was evidence of the formation of amide. A sample grafted with amine-carboxylic acid pairs was three times more active (per free amine) than a sample without such pairs for the nitroaldol condensation of 4-nitrobenzaldehyde and nitromethane.

Keyword: acyloxysilane, Paired bifunctional groups, bifunctional surface, surface modification, cooperative effect.

1. Introduction

Strategic placement of functional groups enables cooperative interaction with molecules, especially in 3-D, and is the basis of the exceptional performance of enzymes as catalysts. Realization of such arrangements could lead to enhancement in substrate activation, selective binding, and transition state stabilization. In spite of its importance, the number of examples where precise placement of multiple functional groups is achieved in synthetic catalysts is limited e.g. [1-8], particularly in heterogeneous systems [8-14].

It is recognized that controlled separation distance between functional groups is essential in order for cooperativity to occur in catalysis [11, 12]. Common methods of surface functionalization often produce random distributions on surfaces, such as the “one-pot” co-condensation of a mixture of tetraorthosilicate functional group precursors, such as the examples in [6], or sequential or concurrent post-synthesis grafting of functional groups, e.g. [7]. These modified bifunctional surfaces have been explored for applications including acid-base catalysis [9, 10], metal ligation [15], and sorption of ions [16]. Introducing a second functional group by post-grafting modification of an anchored precursor can be a more precise positioning method, and this has been employed to generate a carboxylic acid and primary amine pair [17]. Precise positioning is also achieved by activating a grafted precursor to form a pair of covalently linked functional groups, such as a sulfonic acid-thiol pair [11] and amine-carboxylic acid, amine-alcohol, and amine-phosphonic acid pairs [8]. Because the functional groups are covalently attached to the same tether, their relative positions remain unchanged during catalysis.

Another method that has been investigated involves designing a precursor which possesses an internal cleavable bond and terminal end groups for attachment to the surface. Cleaving the internal bond post-grafting generates functional groups separated by the length of the precursor. One example is a molecule that has both a xanthate and a carbamate as cleavable bonds [18], which upon post-grafting thermolysis generate a thiol and an amine, respectively. The relative positions of these functionalities on the surface are predetermined to within the flexibility of the precursor molecule and the tethered fragments after cleavage. A variation of this method is to anchor at two points on the surface a precursor with two different pro-functional groups that can be chemically transformed after grafting into the desired paired catalytic sites [12].

We report here the use of silyl ester bond as another internal cleavable bond to form grafted discrete pairs of functional group on a surface. Compared with the carbamate bond, the silyl

ester (acyloxysilane, $-(C=O)-O-Si-$) bond is readily cleaved by hydrolysis under mild conditions to form a carboxylic acid and an organosilanol pair (distinct from surface silanols). These groups can be readily further converted to other functionalities using known chemistry. Hence, this method can serve as a platform to generate a wide variety of bifunctional catalytic pairs. Using this strategy, we have synthesized and characterized carboxylic acid/amine, carboxylic acid/pyridine, and carboxylic acid/phosphine pairings on a silica surface, and used the Henry reaction between nitromethane and 4-nitrobenzaldehyde to demonstrate their catalytic capability. The differences between paired acid/base groups versus surfaces with randomly dispersed groups were investigated.

2. Materials and Methods

2.1 Materials

All chemical reagents were used as received from either Sigma-Aldrich for organics or Gelest Inc. for Si-containing compounds. A nonporous fumed silica (Cab-O-Sil grade EH-5, 360 m²/g) was used as the support to prevent mass transfer limitations of the large tether molecules into a pore structure. Before grafting, the silica was washed by heating in water at 90°C for 4 h, filtered, and then dried under vacuum at 400°C for 4 h. The temperature was chosen so that the silica surface would be devoid of vicinal silanol groups while maintaining the maximum concentration of isolated silanol groups according to the Zhuravlev model [19] so as to minimize the uncontrolled interaction between adjacent grafted pairs. In the literature, it was reported that such treatment would result in a surface silanol densities of 1.5 SiOH groups per nm² [20-22].

2.2 Synthesis

Error! Reference source not found. shows the synthetic pathway to form the organosilane compound for tethering to the surface followed by subsequent hydrolysis of the internal silyl ester bond. **Error! Reference source not found.** shows the further functionalization of the tethered organosilanol, and **Error! Reference source not found.** shows the synthesis of the mono- and bifunctional surfaces that were used for comparison purposes in the catalytic studies. Detailed syntheses of the compounds shown in these schemes are provided in Supplementary Information. ¹H, ¹³C, and ²⁹Si NMR were the principal tools used to characterize the purity of these compounds. When possible, MS and elemental analyses were also performed. Since all

compounds containing chlorosilane and silyl ester bonds are moisture sensitive, their syntheses and manipulation were performed using the Schlenk technique under N₂ or in a N₂ glovebox. Because of their high hydrolytic sensitivity, only NMR characterization was useful for the chlorosilane compounds. These compounds were used immediately after preparation.

Samples for control experiments were also prepared that contained only tethered –COOH (**Si-COOH**), –NRH (**Si-NH**), and randomly positioned –COOH and –NRH groups (**Random (COOH)(NH)**) using the paths shown in Scheme 3. The details of their syntheses are described in the Supplementary Information.

Scheme 1: Steps in the synthesis of tetrachlorosilylester **III** precursor and subsequent modes of grafting to a silica surface: a) heterofunctional condensation of silyl chloride **I** with acid; b) Karstedt's catalyst catalyzed hydrosilylation; c) condensation with surface silanols; d) hydrolysis of silyl ester bond.

Scheme 2: Functionalization of the organosilanol of **V-D** to create (from right to left) a carboxylic acid/2°amine pairing, a carboxylic acid/pyridine pairing, and a carboxylic acid/diphenylphosphine pairing.

Scheme 3: Synthesis of randomly placed mono- and bifunctional surfaces used in the catalytic studies.

2.3 Characterization

CHN and P elemental analysis were performed by Micro Analysis Inc., Wilmington, DE. Spectroscopic HRMS data were collected with Electron Stimulated Ionization Mass Spectrometer in the IMSERC facility at Northwestern University. ^1H , ^{13}C , ^{29}Si and ^{31}P NMR spectra were collected on a Agilent Au400 MHz spectrometer with a broadband probe. ^{13}C , ^{29}Si , and ^{31}P CP MAS NMR were performed on a Agilent 400 MHz spectrometer with a spin rate of 5000 rpm. Thermogravimetric analysis (TGA) was performed on a TGA/SDTA851 analyzer (Mettler Toledo) in flowing air. X-ray photoelectron spectra (XPS) were collected using Thermo Scientific ESCALAB 250Xi equipped with an electron flood gun and a scanning ion gun, using

Al K α radiation (1486.6 eV) excitation, and adventitious carbon (C1s, 284.8 eV) was used for reference. DRIFTS-IR spectra were recorded on a Nexus 670 equipped with a Harrick's Praying Mantis sample holder at 2 cm⁻¹ resolution using KBr for background subtraction.

The functional groups populating the surface were quantified using transmission IR spectra (Nicolet Nexus 670 FTIR at 4 cm⁻¹ resolution, using KBr for background subtraction). Typically, 5 mg of functionalized silica and 25 mg of KBr were compressed into a 1 cm diameter disk and loaded into a stainless steel IR cell equipped with N₂ gas flow, temperature control, and a NaCl window. Each sample was then subjected to heating at 200°C for 1 hour under flowing N₂ (or until no significant changes in the spectra appeared) in order to removed absorbed water before being cooled to room temperature and the final spectra recorded [23].

2.4 Catalysis Studies

Henry reactions were carried out in a 25 mL Schlenk flask, equipped with magnetic stir bar and rubber septum, in the liquid phase at 50°C under dry N₂ atmosphere. In a typical experiment, 0.030 g of catalyst were added to the flask and then heated under vacuum to 115°C for hours to remove absorbed water. The flask was then cooled to 50°C and filled with N₂ at which point 5 mL of a newly prepared stock solution containing 0.151 g of 4-nitrobenzaldehyde in 20 mL of nitromethane were injected to initiate the reaction (t = 0 min).

The reaction progress was monitored by periodically removing 0.1 mL aliquots of liquid for ¹H NMR analysis. Immediately after withdrawal, each aliquot was diluted with approximately 0.7 mL CDCl₃ and quenched in a water bath at 15°C. The reaction yield and selectivity were obtained through integration of peaks at 10.1 ppm (s, 1H) for the 4-nitrobenzaldehyde, 5.6 ppm (q, 1H) for the β -nitro alcohol product, and 7.72 ppm (d, 2H) for the unsaturated product.

3. Results and Discussion

3.1 Precursor III syntheses and characterization

The key intermediate in this synthesis scheme is the tetrachlorosilane precursor (5-(dichloromethylsilyl)pentanoic acid, 2-((dichloromethylsilyl)ethyl)bis(1-methylethyl)silyl ester (**III**)), that possesses an internal, easily hydrolyzed silyl ester bond and terminal chlorosilane bonds. The ease of its preparation and the flexibility it offers to change the length of the alkyl fragments, degree of branching, and substituents of the chains on either side of the silyl ester

bond are major advantages of this preparation scheme. Since the chains on both sides of the silyl ester bond determine the nature of and the separation between the tethered functional groups, the ability to design them offers substantial control of the modified surface eventually.

The synthesis of **III**, as shown in **Scheme 1**, started with forming the silyl ester bond between 4-pentenoic acid and chlorodiisopropylvinylsilane (**I**) by heterofunctional condensation, catalyzed by triethylamine (TEA) which also served to capture the hydrogen chloride byproduct. After purification, hydrosilylation of **II** with dichloromethylsilane yielded **III**. For illustrative purposes, 4-pentenoic acid was chosen as the starting acid to avoid potential complications of hydrosilylation involving conjugated carbon-carbon double bonds in shorter acids. Longer chain acids result in larger separation distances between grafted carboxylic acid and the organosilanol, but they may also be more susceptible to migratory isomerization of the carbon-carbon double bond.

Compound **I** was used instead of the commercially available chlorodimethylvinylsilane in order to increase steric protection of the silyl ester bonds in **II** and **III** against ligand redistribution around a silyl ester bond, which is known to occur during hydrosilylation [24] [25]. In addition, the vinyl ligand was used in **I** instead of the longer allylsilane homolog because the latter could form a mixture of linear and branched products. These two effects can be illustrated by performing the reactions analogous to those in **Error! Reference source not found.** using chlorodimethylallylsilane and chlorodimethylvinylsilane instead of **I** (results shown in Figure S1).

3.2 Grafting of **III** to silica.

The grafting of **III** to chlorotrimethylsilane-pretreated silica followed established protocols [26]. Attempts to probe whether the silyl ester bond remained intact in the grafted species with ²⁹Si MAS NMR were inconclusive because, for signal-to-noise reasons, a long collection time was needed during which unintended reactions with moisture from air that leaked into the sample tube occurred. Thus, a control experiment was conducted in the liquid phase using triethylsilanol to react with **III** instead of the silanols on silica, and the results showed no evidence of ligand redistribution. The reaction conditions and the results can be found in the Supplementary Information in Section S2, Figure S2. Thus we assume that the backbone of **III** remained intact after anchoring onto the silica surface.

The reaction of **III** with silica could result in either monopodal or dipodal grafting (**Error! Reference source not found.**). In the monopodal form (**IV-M**), chlorosilanes at only one terminal of **III** react with the surface silanol. After hydrolysis of the silyl ester bond, the surface (**V-M**) would be populated with a random distribution of carboxylic acid and organosilanol groups. For the dipodal form (**IV-D**), the chlorosilanes at both terminals of **III** react with the surface. Following hydrolysis and cleavage of the silyl ester bond, an organized pair of carboxylic acid and organosilanol with a predetermined spacing would form on the surface (**V-D**). For the purpose of constructing well-defined bifunctional surfaces, the dipodal form is preferred over the monopodal form. It is expected that the monopodal form would be preferred at high coverages and for structurally rigid precursors.

Thermogravimetric analysis (TGA) was used to distinguish whether the surface was populated mostly by the monopodal (**V-M**) or dipodal (**V-D**) form by comparing the weight loss due to combustion of the samples before and after hydrolysis of the silyl ester bond of the surface species. For **V-D**, the weight loss of the sample before hydrolysis is expected to be about 0.9 times of that after hydrolysis. For **V-M**, however, the weight loss before hydrolysis is 2.5 to 3 times of that after hydrolysis. **Error! Reference source not found.** shows the observed weight loss to be about 11% for the sample before hydrolysis, and 15% after hydrolysis. Correcting for the 2% weight loss of retained water after hydrolysis (estimated from the result of a silica sample without tethers that had been exposed to moisture), the difference in the weight losses is consistent with predominantly dipodal attachment.

Figure 1: TGA analysis showing the weight loss in air of (a) Pretreated silica, (b) **V** (includes both **V-D** and **V-M** if present), and (c) **Paired (COOH)(NH)**.

The ^{13}C CP MAS NMR spectrum of **V-D** is shown in **Error! Reference source not found.a**. The resonances in the range 10 to 20 ppm and -10 to 0 ppm were from the multiple $\text{R}_3\text{SiCH}_2\text{-CH}_3$ and $\text{R}_3\text{Si-CH}_2\text{-}$ groups present. The series of peaks from 20 to 40 ppm were from the carbon atoms on the alkyl chain originated from pentanoic acid. The resonance at ~ 180 ppm was assigned to the carbonyl carbon of the carboxylic acid. No peaks associated with TEA HCl salt were observed in the MAS NMR spectrum, although small amounts of N were detected by elemental analysis of the grafted samples (see Table S1).

Figure 2: ^{13}C CPMAS NMR of: (a) **V-D**, (b) **Paired (COOH)(NH)** (c) **Paired (COOH)(Py)**, and (d) **Paired (COOH)(PPh₂)**.

3.3 Modification of Organosilanol Tether

In order to demonstrate the versatility of this synthesis scheme, three surface bifunctional pairs were synthesized using Scheme 2: **Paired (COOH)(Py)**, **Paired (COOH)(PPh₂)**, and **Paired (COOH)(NH)**.

3.3.1 Paired (COOH)(Py)

Formation of a carboxylic acid/pyridine pair (**Paired (COOH)(Py)**) was accomplished by reacting **V-D** with 3-pyridyldimethylchlorosilane (**VI-B**). The ^{13}C MAS NMR spectrum of **Paired (COOH)(Py)** (**Error! Reference source not found.c**) showed a series of five peaks from ~155 to 120 ppm indicative of the 3-pyridyl moiety. The other ^{13}C signals from -10 to 40 ppm are due to Si-CH₂-CH₂-, Si-CH₃, pyridyl, methylene, and alkyl chains of the carbons associated with the carboxylic acid. Compared to **V-D**, the higher signal intensity for the peak at -2 ppm relative to the others was due to the addition of Si-CH₃ groups from **VI-B**.

The DRIFTS-IR spectrum for **Paired (COOH)(Py)** in Figure S4c showed a new peak at 1582 cm⁻¹ that was absent in **V-D**. It was due to the 8a ring stretching mode of the pyridyl group [27]. Both this 1582 cm⁻¹ and the 1717 cm⁻¹ peak of the C=O stretch were stable to heating to 150°C in flowing He (other than slight shift of the latter to a higher frequency, probably indicating loss of weak hydrogen bonding), whereas the peak at ~1630 cm⁻¹ was removed, suggesting that the latter was due to absorbed water.

From the N content determined by elemental analysis (Table S1), it was estimated that 0.13 mmol of pyridine was condensed onto the surface of 1 g of silica, representing a ~50% conversion of tethered organosilanol in **V-D**. The incomplete conversion of silanols to pyridyl functionalities could be due to steric effect that hinders **VI-B** from accessing the di(isopropyl)silanol of **V-D**.

3.3.2 Paired (COOH)(PPh₂)

The carboxylic acid-phosphine pair was formed by condensation of **V-D** with **VI-C**. Its ^{13}C CP MAS NMR (**Error! Reference source not found.d**) showed the aromatic carbon peaks between 120-140 ppm, together with peaks in the region from -10 to 40 ppm due to remaining carbon atoms of the surface tether. ^{31}P CP MAS NMR was also collected, which showed a single peak at -10.0 ppm and small spinning sidebands that shifted in position with spinning speed. No phosphine oxide peak was observed. The presence of P was also confirmed by elemental analysis (Table S1). From the P content, it was estimated that 0.15 mmol of phosphine was condensed onto 1 g of SiO₂, representing ~62% yield, a quantity likely affected by steric hindrance.

The DRIFT-IR spectrum (Figure S4d) showed a band at 3060 cm^{-1} due to the C–H stretch of the PPh_2 in addition to other C–H stretches in the 2800–3000 cm^{-1} region. A set of new peaks appeared at 1468, 1435, and 1409 cm^{-1} , which could be due to removal of degeneracy of the stretching frequencies at 1591(e_{2g}) and 1482 (e_{1u}) cm^{-1} in monosubstituted benzene rings [28]. A carbonyl stretching band at 1717 cm^{-1} was also present.

3.3.3 Paired (COOH)(NH)

The carboxylic acid/secondary amine pairing was achieved by reaction of organosilanol in **V-D** with N-methyl-aza-2,2,4-trimethylsilacyclopentane (**VI-A**). The silazane (Si-N) bond was quite labile and reacted readily by ring opening with both COOH and Si–OH moieties present on the surface [29]. Reaction with $\equiv\text{Si-OH}$ would result in the formation of a tethered secondary amine. However, reaction with COOH would form a new silyl ester that would be cleaved upon exposure to water to regenerate COOH during purification. **Error! Reference source not found.** shows a ^{13}C CPMAS NMR spectrum of **Paired (COOH)(NH)** Compared with the spectrum of **V-D**, the intensity for peaks in the range from 20 to 40 ppm increased due to the increased number of alkyl carbons and $\text{R}_3\text{SiCH}_2\text{-CH}_3$ groups. Also, a broad peak appeared at 50–60 ppm, consistent with the presence of secondary amine in the sample.

Elemental analysis showed the presence of 0.52 wt.% N in the sample (Table S1). This corresponded to 0.27 mmol of N per g SiO_2 , which was within experimental error of 0.24 mmol based on the amount of cyclic silazane reacted.

Compared to **V-D**, the peak intensity at 1700–1800 cm^{-1} in the DRIFT-IR spectrum was much lower (Figures S4). A new, broad peak which is a combination of several overlapping peaks appeared at $\sim 1630 \text{ cm}^{-1}$, and the intensity of the very broad, low intensity peak at 3000–3300 cm^{-1} increased. In addition to the $\sim 50\%$ lower intensity, the C=O stretching band was shifted from $\sim 1740 \text{ cm}^{-1}$ in **V-D** to $\sim 1720 \text{ cm}^{-1}$ in **Paired (COOH)(NH)**. This drop in intensity was much more prominent than the $\sim 20\%$ reduction for the other bifunctional modifications (**Paired (COOH)(Py)** and **Paired (COOH)(PPh₂)**). The frequency shift of the carbonyl stretch might be due to hydrogen bonding between amine and carboxylic acid, implying that the flexible -COOH and -R₂NH tethers were in close proximity to each other. We could not detect the characteristic C–N stretching at $\sim 1190 \text{ cm}^{-1}$ due to highly intense Si–O–Si vibrations in that region.

Unlike the peak at $\sim 1630\text{ cm}^{-1}$ observed with **Paired (COOH)(Py)**, this peak could not be removed by heating to 150°C in flowing He. Thus it was not due to adsorbed water. Together with its absence in **Paired (COOH)(PPh₂)**, the presence of a thermally stable ($>150^{\circ}\text{C}$) broad peak at $3000\text{-}3300\text{ cm}^{-1}$, and the fact that carboxamides are known to have peaks between $1600\text{-}1700\text{ cm}^{-1}$ [30], we assigned this peak to the formation of a tertiary amide between the tethered secondary amine and the COOH. Recently, it has been reported that direct thermal condensation can occur in quantitative yields for certain carboxylic acids and amines in toluene at temperatures as low as 110°C [31], which is lower than the drying temperature of 150°C of our samples. Thus, it is conceivable that carboxamides are being formed through the direct thermal condensation. Alternatively, the carboxamide could be formed by reaction of an activated carboxylic acid and an adjacent amine. It has been reported carboxylic acid could be activated by reaction with phenylsilane [32] or tetrakis(pyridine-2-yloxy)silane [33] to form silyl esters which coupled with amines to form amides. In the case of **Paired(COOH)(NH)**, the carboxylic acid could have been activated by reaction with silazane to form the silyl ester, which reacted with a nearby amine to form an amide.

We demonstrated that amide can be formed by monitoring the reaction of pentanoic acid with an equimolar quantity of **VI-A** at 100°C . As can be seen in Figure S6, a strong peak at 1647 cm^{-1} that cannot be attributed to either reactant emerged after 20 h, indicating the formation of a new chemical bond. Furthermore, we found that the reaction of pentanoic acid with either triethylamine or diethylamine did not result in a peak at $\sim 1630\text{ cm}^{-1}$. Thus, the formation of an ion pair (carboxylate ammonium) was not the origin of this peak.

It is essential to quantify the amount of amide formed, since its formation effectively removed a carboxylic acid/ 2° amine pair from the surface. Unfortunately, attempts to quantify this using the N1s peak in XPS were unsuccessful (spectra in SI). Thus, the IR peak intensities indicative of carboxylic acid ($\sim 1720\text{ cm}^{-1}$), amide ($\sim 1630\text{ cm}^{-1}$), and carboxylate ($\sim 1575\text{ cm}^{-1}$) groups were used to calculate the relative amounts after correcting for their different extinction coefficients (Figures S7 and S8). The amount of amine was set equal to the sum of carboxylic acid and carboxylate ions. Together with the total N content from elemental analysis, the quantity of amide could be calculated. These results are summarized in Table 1. As expected, there were more amide formed in **Paired (COOH)(NH)** than in **Random (COOH)(NH)** because the COOH and amine groups were in closer proximity to each other on average in the

former sample. Interestingly, carboxylate formation was minor in both samples, which implied that neutralization of amine and carboxylic acid was not a serious problem.

Table 1: Quantity of surface functional groups.

	Amine	Amide	COOH	COO ⁻
Sample	(mmol/g)	(mmol/g)	(mmol/g)	(mmol/g)
Paired (COOH)(NH)	0.057 ^a	0.213 ^b	0.049	0.008
Random (COOH)(NH)	0.085 ^a	0.185 ^b	0.062	0.023
Si-NH	0.180	--	--	--

Footnote:

a. From the preparation method, which dictates equal amounts of NH and carbonyl groups, and the fact that formation of amide consumes equal amounts of carboxylic acid and amine, the quantity of amine must equal sum of carboxylic acid and carboxylate.

b. Total amount of amine and amide determined from N content in the sample from elemental analysis.

3.4 Henry Reaction

Samples **Si-COOH**, **Si-NH**, **Paired (COOH)(NH)**, and **Random (COOH)(NH)** were evaluated as catalysts for the Henry reaction of 4-nitobenzaldehyde with nitromethane at 50°C (Scheme 4) to form β -nitroalcohol and β -nitroalkene as the major products. Sample **Si-COOH** showed no activity. The other three samples were all active, but the **Paired (COOH)(NH)** was the most active, whereas **Si-NH** was the least active. They all produced nitroalcohol with high selectivity, as shown in Table 2. The formation of nitroalcohol involves amine abstraction of a proton from nitromethane too from an ion-pair intermediate, which subsequently reacts with the aldehyde to form nitroalcohol. In samples where carboxylic acid groups are present, these groups can stabilize the charged transition state in the very nonpolar environment of our silylated surface, enhancing the reaction rate.

The selectivities for nitroalcohol ranged from ~95% for **Random (COOH)(NH)** and **Si-NH** to 86% for **Paired (COOH)(NH)**. Since the selectivity did not change with reaction time, β -nitroalkene must be a primary product formed in a parallel reaction pathway and not by sequential dehydration of β -nitroalcohol. This agrees with an earlier report of Bass *et al.* who

did not observe interconversion between β -nitroalcohol and β -nitroalkene in the presences of a primary amine-silanol bifunctional catalyst [34]. These authors further observed that catalysts containing amine are much more selective for β -nitroalcohol formation than those containing amine-silanol pairs, and postulated that β -nitroalcohol is formed via an ion-pair mechanism, whereas β -nitroalkene is formed via an imine intermediate.

Scheme 4: Henry reaction (nitroaldol condensation) of 4-nitrobenzaldehyde and nitromethane to form a β -nitroalcohol and β -nitroalkene.

The high nitroalcohol selectivity observed in this study with the **Si-NH** sample is consistent with the observation of Bass et al. However, although somewhat lower in selectivity, nitroalcohol remained the dominant product for **Paired (COOH)(NH)**, which differs from the observation of nitroalkene being the dominant product for primary amine-silanol pairs [34]. We believe that the difference could be due to the fact that our samples contain the more basic secondary amine that readily favors the abstraction of proton from the nitromethane that leads to nitroalcohol formation, while its steric bulk might hinder nucleophilic attack on the nitrobenzaldehyde to form an imine and then nitroalkene.

Table 2: Initial turnover frequency and selectivity of catalysts studied.

Catalyst	Initial TOF ^a (h ⁻¹)	Conversion after 24 h (%)	Nitroalcohol Selectivity (%)
Si-NH	6.8	93	94
Random (COOH)(NH)	10.3	70	95
Paired (COOH)(NH)	22.8	87	86

Footnote:

a. Estimated after ~4 h of reaction, calculated assuming that both neutral and protonated amine groups are potential active sites.

4. Conclusion

We have demonstrated that a new, siloxane-based precursor molecule with an internal silyl ester bond can function as a useful and versatile platform for the synthesis of bifunctional surfaces. The synthesis method makes use of the demonstrated versatility in modifying silanol groups to form different functionalities. The stability of siloxane and the ease to manipulate the chain length and addition of side chains and functionalities with known siloxane chemistry make this an attractive method to engineer designed surface architecture for various applications. Using one such precursor molecule, surfaces that possess four pairs of functional groups were constructed: carboxylic acid/silanol, carboxylic acid/amine, carboxylic acid/pyridine, and for the first time, carboxylic acid/phosphine that represent pairs of different properties, ranging from acid/acid, acid/base, to acid/nucleophile. Not only that the chemical nature of the pairs can be tuned, the separation distance between the groups can be adjusted based on the design of the precursor molecule. It should be quite feasible to construct mono-, bi-, and tridentate silylated phosphines using this method. This is a new pathway for catalyst immobilization, particularly with mixed ligand systems. The surface tethered acid can also function as a promoter for many reactions reducing the need for large excess liquid phase organic acids.

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