Surface Science 648 (2016) 284–290

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Synthesis and characterization of bifunctional surfaces with tunable functional group pairs

John M. Galloway, Mayfair Kung, Harold H. Kung *

Department of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208, USA

A R T I C L E   I N F O

Available online 20 October 2015

Keywords:
Acyloxysilane
Paired bifunctional groups
Bifunctional surface
Surface modification
Cooperative effect

A B S T R A C T

Grafting of pairs of functional groups onto a silica surface was demonstrated by tethering both terminals of an organochlorosilane precursor molecule, $Cl_2(CH_3)Si(CH_2)_4(CO)(OSi(i\text{-}Pr)_2)(CH_2)_2Si(CH_3)Cl_2$, 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.

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.

---

* Corresponding author.
E-mail address: hkung@northwestern.edu (H.H. Kung).

http://dx.doi.org/10.1016/j.susc.2015.10.004

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 m^2/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 nm^2 [20–22].

2.2. Synthesis

Scheme 1 shows the synthetic pathway to form the organosilane compound for tethering to the surface followed by subsequent hydrolysis of the internal silyl ester bond. Scheme 2 shows the further functionalization of the tethered organosilanol, and Scheme 3 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. ^{1}H, ^{13}C, and ^{29}Si 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 N_2 or in a N_2 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.

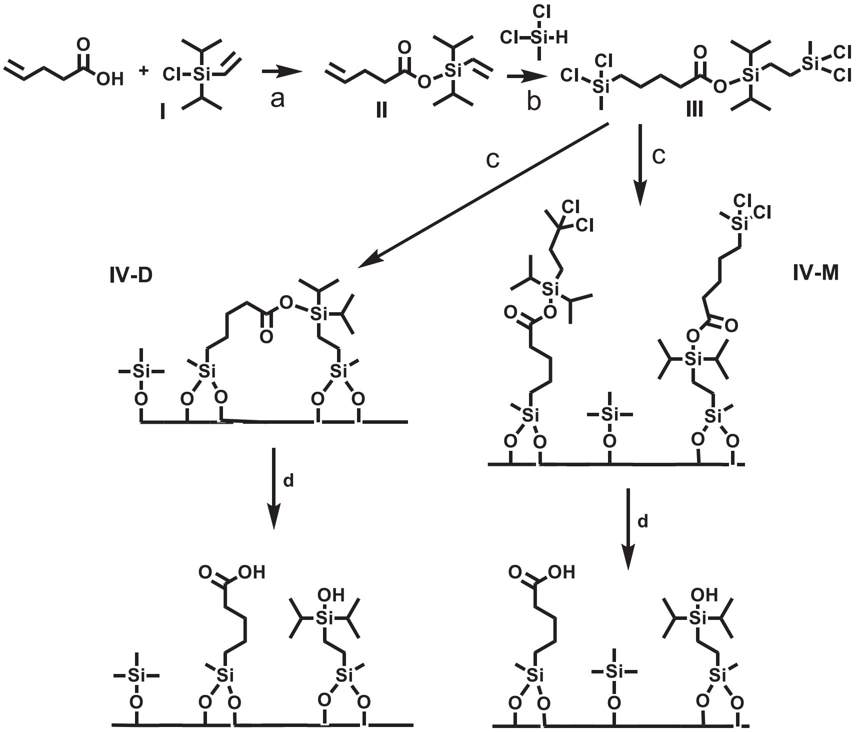
2.3. Characterization

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. ^{1}H, ^{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 Kα 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 N_2 gas flow, temperature control, and a NaCl window. Each sample was then subjected to heating at 200 °C for 1 h under flowing N_2 (or until no significant changes in the spectra appeared) in order to remove 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



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; and d) hydrolysis of silyl ester bond.