Oligomerization of trimethylsilyl acetylene to form large molecules on reduced surfaces of TiO$_2$(0 0 1)

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Abstract

The catalytic cyclotrimerization of alkynes on reduced TiO$_2$(0 0 1) surfaces has been explored to probe the active sites for carbon–carbon bond formation. The influence of surface–adsorbate interactions on the reaction mechanism was further probed by studies designed to characterize the steric effects of differently functionalized alkynes. The chemistry of trimethylsilyl acetylene on surfaces containing Ti^{2+} sites clearly demonstrates that cyclotrimerization of heteroatom-containing alkynes is feasible. Trimethylsilyl acetylene can be cyclized to form tris-(trimethylsilyl)-benzene on the reduced titania surface. However, the principal product on both reduced and stoichiometric surfaces of TiO$_2$(0 0 1) is the hydrogenation product, trimethylvinylsilane (TMVS). The low yield of oligomeric products is attributed to the steric effect of the bulky trimethylsilyl group. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Oligomerization; Trimethylsilyl acetylene; Reduced TiO$_2$(0 0 1) surfaces

1. Introduction

Among the basic principles that have arisen during the study of semiconducting metal oxide surface chemistry is the critical role played by the coordination and redox environment of surface metal cations. Product selectivity is often governed by the electronic properties of the metal cationic center. This has been demonstrated on a variety of metal oxides such as TiO$_2$, with a host of different reactions. Examples include structure-specific ketonization of acetic acid [1] and oxygen vacancy dependent reductive coupling of aldehydes [2]. In fact, for carefully chosen crystal faces, some of these examples have mirrored selectivity trends demonstrated on polycrystalline samples of the same material [3].

In general, the evidence suggests that selectivity toward a particular product is dependent on the interplay of surface–adsorbate and adsorbate–adsorbate interactions. Resolution of the relative influences of these interactions is important to understand and extend the chemistry of reaction intermediates. Studies of the product selectivities for reactions among families of reactants have provided insights into these interactions. An example is the difference in etherification yields between primary and secondary alcohols on TiO$_2$(0 0 1) surfaces [4].

We have chosen to study these interactions by carrying out the cyclotrimerization of substituted alkynes on reduced and stoichiometric TiO$_2$(0 0 1) surfaces. Alkynes readily cyclotrimerize on surfaces possessing Ti^{2+} cations [5]. The stoichiometric TiO$_2$(0 0 1) surface is inactive for alkyne cyclotrimerization and only forms hydrogenation products. Efforts to identify the reaction intermediate have focused on metallacyclopentadiene structures in which a C$_4$H$_4$ ligand is

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anchored to the titanium metal cation at both ends. Experiments have shown that this is the most probable structure; for example, comparisons between the reactivity of methyl acetylene and its isomer, allene, have demonstrated that cyclotrimerization products are only formed from the alkyne precursor [6]. Likewise, experiments with cyclooctatetraene ruled out metallacyclopentadiene dimerization as a step in cyclotrimerization [7]. In addition, the exclusivity of the cyclotrimerization reaction to surfaces containing Ti^{2+} cations suggests that only one important surface intermediate is likely. Definitive spectroscopic identification of the metallacyclopentadiene on titanium oxide surfaces has proven elusive, but the evidence to date is entirely consistent with this species. Cyclotrimerization of bulky alkynes provides a useful model reaction to probe steric effects in synthetic chemistry on oxide surfaces.

Alkyne cyclotrimerization has been studied extensively in homogeneous catalysis. Many Group VIII transition metals catalyze this reaction, including Co, Rh, and Ir [8,9]. The mechanism is dependent on two-electron cycling of the metal center. Iridium, for example, cycles between Ir^+ and Ir^{3+} as it forms the aromatic cyclotrimer. Oxidative addition of two alkynes to the metal center creates a metallacyclopentadiene intermediate, which has been identified through X-ray crystallography for several catalytic systems. Reductive elimination of the cyclic aromatic product causes the metal center to revert to the original oxidation state, completing the catalytic cycle. The nearly identical dependence on Ti^{2+} for the heterogeneously catalyzed reaction on $TiO_2(0\,0\,1)$ provided a basis for the proposal of the metallacyclopentadiene intermediate discussed earlier for this surface reaction [5]. The separation of metal cations from one another on the metal oxide surface has been suggested to provide a reaction environment analogous to that of mononuclear metal complexes in solution. This provides a rational basis for the mechanistic analogy between solution and surface chemistry [10].

2. Experimental

The VG ESCALAB Mark II vacuum system used in these experiments has been described previously [7]. A 10 mm × 10 mm, (0 0 1)-oriented single crystal of TiO_2 was utilized in this system throughout this investigation. The crystal was mounted on a three-motion sample probe attached to the chamber by a rotational stage. The main shaft of the sample probe was hollowed out to allow intimate contact of liquid nitrogen with the crystal mount. This method of cooling provided a base temperature of 150 K for the titania crystal; resistive heating of the sample mount allowed the temperature to be raised to 900 K for temperature programmed desorption (TPD) experiments. Reduced surfaces of the single crystal sample were created by argon ion bombardment at 2 keV for 60 min; the current flux was typically $3.5\,\mu A\,cm^{-2}$. Less reduced surfaces were created by annealing the crystal after bombardment. Restoration of the stoichiometric surface required annealing at 900 K for 45 min. The sputter-generated Ti^+, Ti^{2+}, Ti^{3+}, and Ti^{4+} surface cations were identified and quantified with X-ray photoelectron spectroscopy (XPS) [5].

Adsorption of trimethylsilyl acetylene on the single crystal surface was accomplished by 1 min exposure at 190 K with a capillary dosing needle aimed directly at the crystal surface at a distance of less than 5 mm. The background pressure of the chamber was measured as 2×10^{-9} mbar throughout the dose. Our experience suggests that an order of magnitude increase in exposure may be achieved when compared to indirect methods. While the direct-exposure method precludes exact exposure determination, it provides a fast route to saturation coverage with a minimum amount of time needed to re-establish nominal background pressure (typically 6×10^{-11} mbar).

Reaction and desorption of trimethylsilyl acetylene during TPD were monitored with a quadrupole mass spectrometer (Hiden HAL 511) enclosed in a differentially pumped quartz shroud. Thirty masses were tracked during the experiments to identify the desorbing products. Product assignment was based on mass fragmentation patterns where possible; literature patterns were substituted when commercial samples were not available for experimental verification.

Product quantification was based on area integration of mass spectra corrected for differences in ionization using the method developed by Ko et al. [11]. Product yields were defined in relation to the amount of chemisorbed carbon detected with XPS on the sputtered surface after reactant adsorption and heating of

Table 1
Product mass fragmentation patterns used in analyzing TPD experiments[a]

Mass	TMSA (measured)	Trimethylsilane [19]	1,2,4-tris-(trimethylsilyl)-benzene [19]	TMSA dimer (measured)	Trimethylvinylsilane (measured)
45	18.6	9.4	29.3	96.7	25.7
53	100.0	3.0	1.6		7.7
59	10.0	**100.0**	10.0		100.0
67	49.0	0.5	1.1		2.2
73	4.0	55.4	100.0	100.0	13.5
84	46.0				0.6
85	27.0		1.1		**74.5**
95	0.1		3.3	23.9	
98	**24.0**		0.2		
99	3.0		0.8	**7.3**	0.1
112				6.9	
113				3.6	
124			21.0	1.2	
157				28.0	
263			6.5		
279			**34.0**		
294			6.5		

[a] Diagnostic masses are denoted with bold type.

the surface to remove physisorbed layers. Table 1 lists the cracking patterns used to analyze TPD data.

3. Results and discussion

3.1. Temperature programmed desorption

Trimethylsilyl acetylene (TMSA, parent mass = 98 amu) desorbs from three adsorbed states. Fig. 1 illustrates these states for TMSA adsorbed on the stoichiometric $TiO_2(0\,0\,1)$ surface at different exposure levels at 150 K. The large feature at 165 K shifts down in temperature with increasing exposure. This peak is attributable to TMSA desorption from a condensed state on the crystal surface. A desorption peak at 225 K becomes saturated as the exposure level increases, evidence for a molecularly chemisorbed state. Similarly, a broad desorption peak arising from another chemisorbed state exists with a peak temperature of 265 K, which has been expanded in Fig. 1 for clarity.

Previous examples of alkyne cyclotrimerization chemistry on the $TiO_2(0\,0\,1)$ surface demonstrated a clear correspondence between the availability of Ti^{2+} cations on the surface of the crystal and

the production of the cyclotrimer and intermediate dimers. Surfaces annealed to lower temperatures after sputtering (and therefore containing Ti^{2+} cations) produced the cyclotrimer corresponding to TMSA, tris-(trimethylsilyl)-benzene. Surfaces annealed to
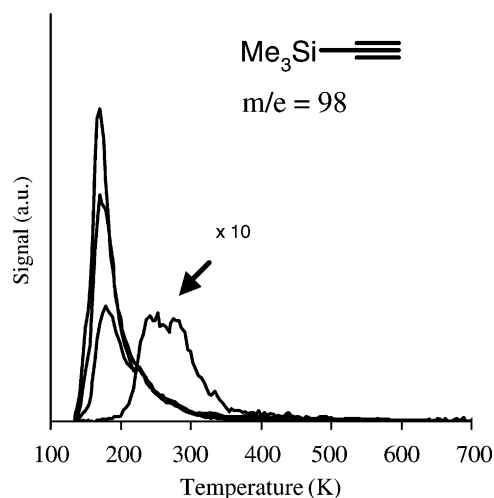

Fig. 1. Condensed TMSA on stoichiometric $TiO_2(0\,0\,1)$. Increasing exposure of trimethylsilyl acetylene (TMSA) on the stoichiometric $TiO_2(0\,0\,1)$ surface at 150 K reveals desorption from a multilayer state at 165 K and molecular desorption features at 225 and 265 K.

temperatures high enough to eliminate surface Ti^{2+} sites did not produce coupling products at all. Fig. 2 illustrates the surface populations of titanium cations from analysis of the Ti (2p) photoemission region with XPS [7]. As the sputtered $TiO_2(0\,0\,1)$ surface is annealed at increasingly higher temperatures, the population of low-valent titanium cations decreases sequentially. This behavior permits the creation of tailored $TiO_2(0\,0\,1)$ crystal surfaces with reproducible populations of Ti^{2+} cations.

The cyclotrimer of TMSA, tris-(trimethylsilyl)-benzene (parent mass $= 294\,amu$), was formed on surfaces containing Ti^{2+} cations, and was tracked during TPD experiments using $m/e = 279$ as a diagnostic mass, as it exhibits a more intense signal than the parent mass. Examination of the TPD spectrum for a surface sputtered and annealed to 400 K (Fig. 3) reveals that the cyclotrimer desorbs in a broad peak between 320 and 520 K with a peak temperature of 430 K. Identification of the cyclotrimer was made by comparing features of this
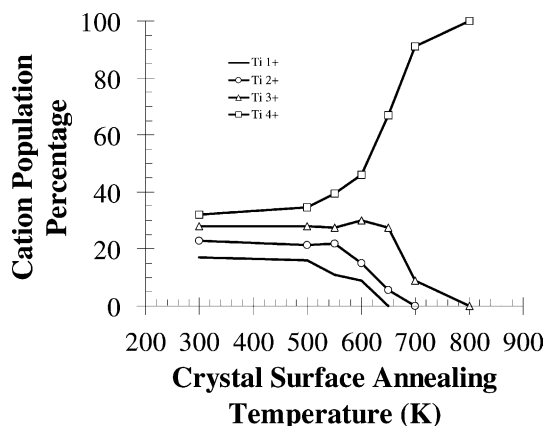

Fig. 2. Surface titanium cation population for sputtered and annealed $TiO_2(0\,0\,1)$. The population of titanium cations at the surface is mapped as a function of the post-sputter annealing temperature. Low-valent surface cations are sequentially re-oxidized by thermal annealing to successively higher temperatures.
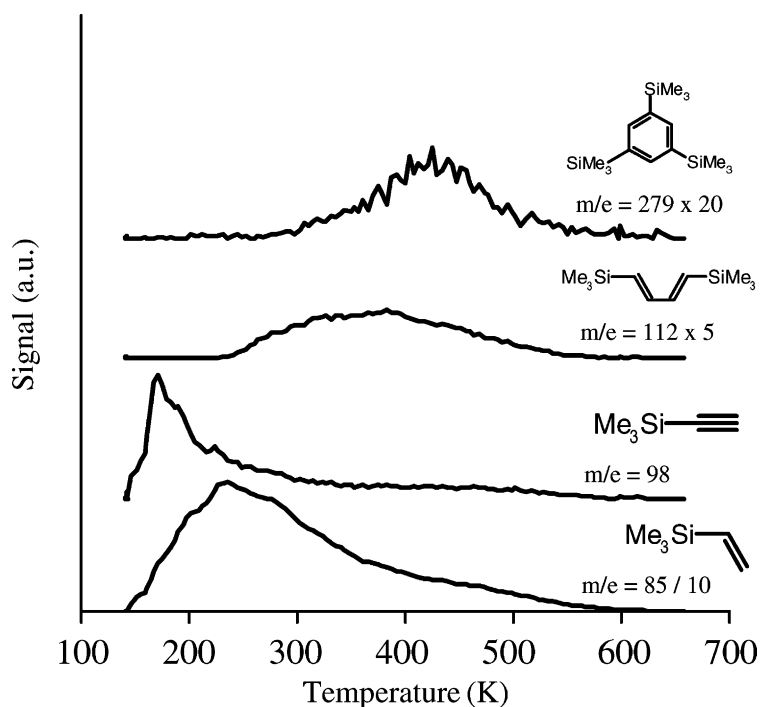

Fig. 3. TMSA TPD on sputtered $TiO_2(0\,0\,1)$, showing desorption of the cyclotrimer, dimer, and hydrogenation products as well as the parent molecule. The oligomer structures shown are simply meant to represent generic dimer and cyclotrimer products, not specific isomers.

peak with a literature mass fragmentation pattern for 1,2,4-tris-(trimethylsilyl)-benzene (the only literature pattern available—see Table 1). While the cracking pattern is not an exact match, the relative proportions of the signature features at large masses confirm the presence of the cyclotrimer product.

All prior studies of alkyne cyclotrimerization on reduced $TiO_2(0\,0\,1)$ surfaces have also identified the production of dimers as well as cyclotrimers. Dimer production has been explained as the result of hydrogenation of the proposed metallacyclopentadiene intermediate competing with insertion of the final monomer to complete the ring. For TMSA, another oligomeric product desorbed over roughly the same temperature range as the cyclotrimer, and was tentatively identified as bis-(trimethylsilyl)-butadiene, the hydrogenated dimer product of TMSA. Identification and quantification of the TMSA dimer was based on a cracking pattern synthesized from TPD traces after subtraction of all other products. Fig. 3 depicts the spectrum for $m/e = 112$ to highlight dimer production; the mass used for calculating the dimer yield was $m/e = 99$.

Trimethylvinylsilane (TMVS, parent mass $=$ 100 amu, diagnostic $m/e = 100$) desorbed at 230 K in a broad peak, coincident with another product, trimethylsilane (TMS, parent mass $=$ 74 amu, diagnostic $m/e = 59$). Both are produced by hydrogenation of TMSA. Hydrogenation of the reactant alkyne is the primary side reaction for all alkyne cyclotrimerization reactions studied on reduced surfaces of $TiO_2(0\,0\,1)$ thus far. The formation of TMSA hydrogenation products is also the dominant reaction in the present case, accounting for just over 75% of the yield from the reduced surface. The hydrogenation reactions and their contributions to the TMSA product slate will be discussed further below.

A contaminant, hexamethyldisiloxane, was also detected at an apparent yield of less than 4%. Hexamethyldisiloxane is a decomposition product of TMSA, and is likely to have formed in the dosing manifold prior to adsorption. Although not reproduced here, experiments with varying exposure of TMSA demonstrated that hexamethyldisiloxane was coadsorbed with TMSA, and was not a reaction product of TMSA on the surface. The conclusion was supported as well with TPD, which showed a narrow,
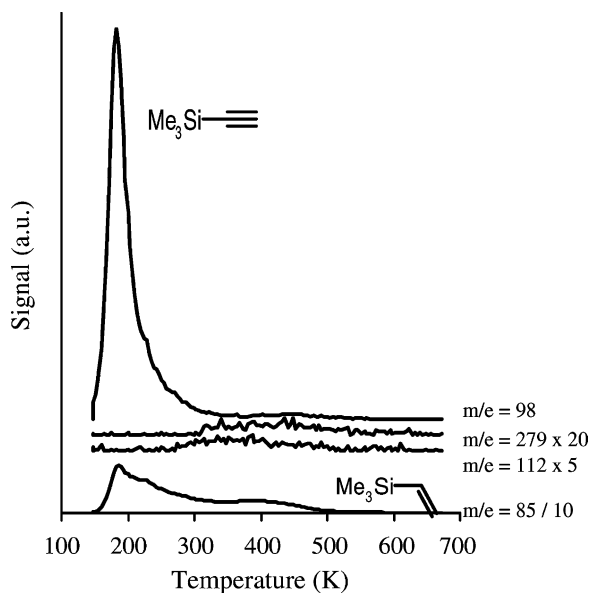

Fig. 4. TMSA TPD on stoichiometric $TiO_2(0\,0\,1)$. No oligomeric products are formed on the stoichiometric surface; only hydrogenation products are generated from adsorption and reaction of TMSA.

low-temperature desorption peak for the contaminant, as well as roughly constant yields of TMSA and hexamethyldisiloxane for all surfaces studied.

Comparison of the these TPD features with those from TMSA adsorption and reaction on the sputtered surface annealed to 800 K (Fig. 4) reveals a complete change in the surface chemistry, as expected on the stoichiometric surface. About half of the TMSA that sticks to the surface desorbs as the parent molecule, desorbing at 165 K. The remaining molecules are hydrogenated, forming TMVS and TMS, which desorb at 220 K. No oligomeric products are generated on the stoichiometric surface.

3.2. X-ray photoelectron spectroscopy

The carbon (1s) spectrum of multilayers of trimethylsilyl acetylene on the stoichiometric $TiO_2(0\,0\,1)$ surface is shown in Fig. 5. This spectrum can be fit with three peaks with binding energies of 286.2, 287.1, and 288.0 eV. The respective area ratio for these peaks is 1:2.8:1.1. Three of the five carbons in TMSA are methyl group carbons and should be
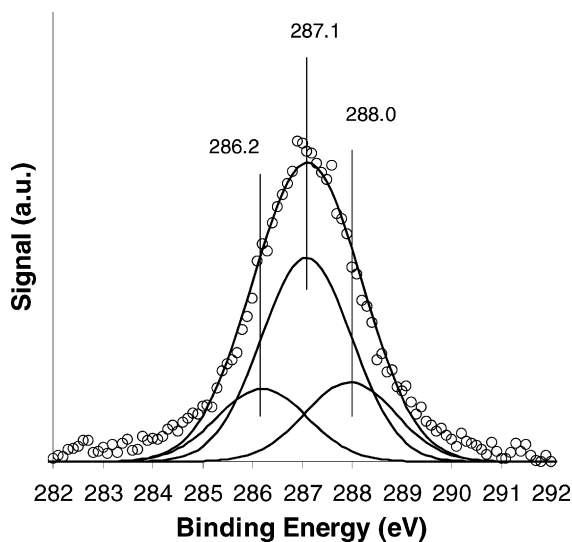
Fig. 5. Carbon (1s) XPS of condensed multilayers of TMSA on stoichiometric $TiO_2(0\,0\,1)$. The peaks at 286.2, 287.1, and 288.0 eV have been assigned to carbon atoms in the HC≡, H_3C–, and Si–C≡, respectively.
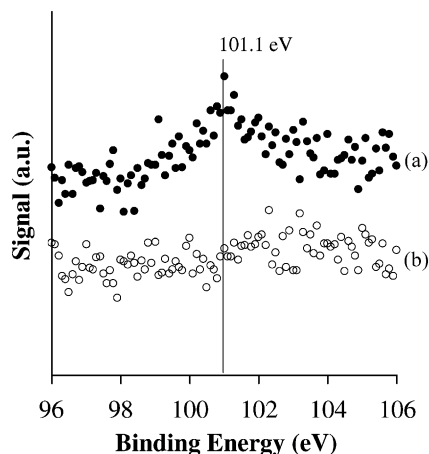

Fig. 6. Silicon (2p) XPS of TMSA adsorbed on the reduced surface of $TiO_2(0\,0\,1)$. The top spectrum was collected after heating a TMSA-saturated surface to 220 K; the bottom spectrum was collected after heating that surface to 650 K.

indistinguishable from each other. The remaining acetylenic carbons have different electron densities, as one is attached to a hydrogen atom while the other is bound to the silicon atom. Studies of methyl acetylene condensed on Ag(1 1 0) surfaces (an inactive surface, much like stoichiometric $TiO_2(0\,0\,1)$) have suggested that, of the three carbon atoms in that molecule, the acetylenic carbon adjacent to the methyl group is the most electron-deficient [12]. Therefore, that carbon exhibits a higher C (1s) binding energy than those of the methyl carbon and the terminal acetylenic carbon. Similarly, it may be argued that the acetylenic carbon attached to silicon is more electron-deficient than carbon in the methyl groups. The near 1:3:1 ratio of the XPS features in the spectrum may be assigned as HC≡, H_3C–, and Si–C≡ in order of increasing binding energy.

Trimethylsilyl acetylene was adsorbed on the reduced surface at 160 K and heated to 220 K to remove physisorbed layers. The silicon (2p) XPS spectrum obtained is shown in Fig. 6(a). A low intensity peak is centered at 101.1 eV, with a FWHM of 1.7 eV. The position of this emission feature is consistent with that reported for tetraphenylsilane [13–15]. The crystal was heated to 650 K at $1\,K\,s^{-1}$ to simulate a

TPD experiment, and XPS was collected again after cooling (Fig. 6(b)). The surface appeared to be free of silicon, although XPS is not particularly sensitive to silicon [14].

Carbon (1s) spectra before and after the TPD heating cycle are shown in Fig. 7. The parent TMSA molecule and the hydrogenation products are mostly gone from the surface by 220 K, leaving a surface
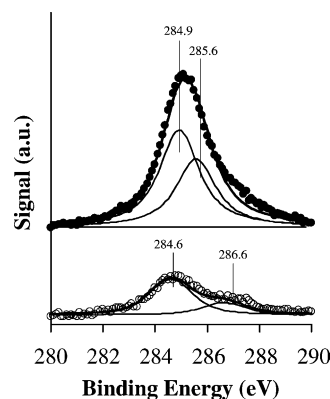

Fig. 7. Carbon (1s) spectra for TMSA on reduced $TiO_2(0\,0\,1)$. The top spectrum was collected after heating a TMSA-saturated surface to 220 K. The ratio of peak areas is about 3:2, consistent with the distribution of carbon types in the product; the bottom spectrum represents that surface heated to 650 K.

containing mainly oligomeric species. Peaks fitted to the XPS data were guided by the expected molecular structures; thus, peak width (2.0 eV) and peak area ratios (methyl:non-methyl carbons = 3:2) were fixed and the binding energy was optimized by the peak-fitting routine. Unlike the multilayer TMSA spectrum, the chemisorbed layer of TMSA at 220 K reveals peaks at 284.9 and 285.6 eV. The chemisorbed layer features exhibit a relaxation shift of 2.2 eV when compared to those of the multilayer spectrum. The C (1s) peaks for acetylides formed from methyl acetylene and acetylene on Ag(1 1 0) increased in energetic separation when compared to their molecular counterparts [12]. This is consistent with a vertical orientation of the acetylide, where one carbon does not interact with the surface and cannot benefit from further relaxation. For TMSA at 220 K, the peak spacing between methyl group carbon and acetylenic carbon bound to silicon is similar (0.7 versus 0.9 eV in the condensed layer spectrum). It is likely that the 220 K spectrum has captured the dimer or cyclotrimer. The two peaks have an area ratio of 3:2, which corresponds to the 3:2 ratio of methyl to ring or backbone carbons in the oligomers.

Seventy-five percent of the carbon present on surface before TPD desorbed by 650 K. Two distinct carbon peaks remain in the XPS spectrum following heating to 650 K. The first, at 284.6 eV (FWHM = 2.0 eV), accounts for three-quarters of the carbon photoemission area in the post-TPD spectrum, and likely represents residual carbon from decomposition (perhaps as the result of hydrogen transfer reactions to form trimethylsilane). The remaining area appears as a peak at 286.6 eV (FWHM = 2.0 eV). This feature may be due to carbon oxides formed during decomposition of the hexamethyldisiloxane contaminant or residual carbon–silicon species. Unfortunately, XPS is not sensitive enough to rule out the presence of silicon on the surface after heating to 650 K.

The C (1s) spectrum on the stoichiometric surface at 220 K is qualitatively similar to the spectrum of residual carbon on the sputtered surface at 650 K (Fig. 8). Peaks at 284.5 and 286.6 eV (FWHM = 2.0 eV) have an area ratio of 4:1. Since no cyclotrimer or dimer is formed on the stoichiometric surface and the hydrogenation products had mostly desorbed by 220 K, it is likely that these features represent
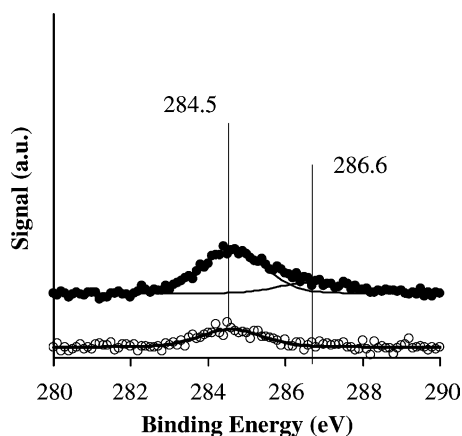

Fig. 8. Carbon (1s) XPS of TMSA adsorbed on stoichiometric TiO$_2$(0 0 1). The top spectrum was collected after heating a TMSA-saturated surface to 220 K; the bottom spectrum was collected after heating that surface to 650 K.

decomposition products of the hexamethyldisiloxane contaminant or decomposed TMSA. Sixty-five percent of the surface carbon has desorbed by 650 K, and only the peak at 284.5 eV remains. The silicon (2p) region (not shown) appeared flat for the oxidized surface heated to both 220 and 650 K, consistent with desorption of most of the silicon-containing molecules (e.g. TMSA, TMVS, and TMS) below these temperatures.

4. Discussion

Trimethylsilyl acetylene reacts on the reduced TiO$_2$(0 0 1) surface to form four main volatile products, two of them being oligomers. The reaction network on reduced surfaces is shown schematically in Fig. 9. Comparison of the results of the present work with those of our previous studies of less bulky reagents demonstrates that the functional groups attached to the acetylenic carbons affect both the conversion and selectivity of alkyne reactions. Fig. 10 illustrates the relative product yields calculated for each of the alkynes studied on reduced TiO$_2$ surfaces to date. In the case of TMSA, hydrogenation products dominated the desorbing species from sputtered and stoichiometric TiO$_2$(0 0 1) surfaces—over 75% of the yield from the sputtered surface annealed
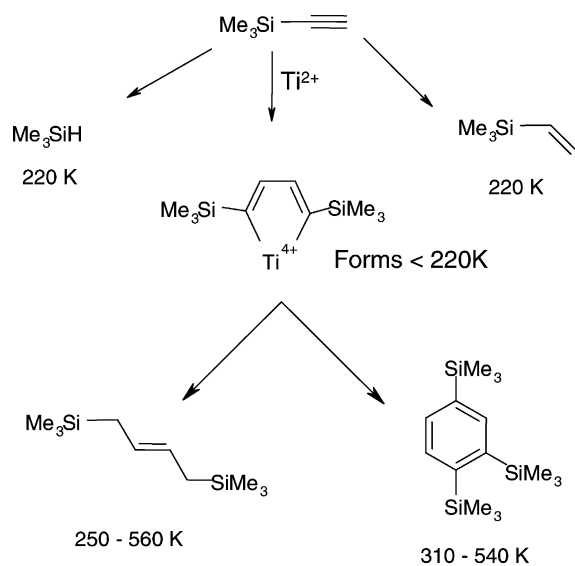
Fig. 9. Schematic of reaction pathways for TMSA on the reduced surface of TiO$_2$(0 0 1).

to 400 K was composed of trimethylvinylsilane and trimethylsilane. Oligomeric products (the dimer and the cyclotrimer) were produced at around 21% yield on the most reduced surface, and monotonically declined in yield as the crystal surface became more oxidized. The correspondence between the Ti^{2+} population and the production of oligomers is illustrated in Fig. 11, where it is evident that the Ti^{2+} metal cations are necessary to form carbon–carbon bonds.

The generation of hydrogenation products in excess of that expected from parent molecule decomposition has been demonstrated in earlier alkyne cyclotrimerization experiments on the reduced surface. The hydrogen source is likely to be the surface, which picks up hydrogen during the sputtering process. The role of the hydrogenation reaction is difficult to determine. Several alkynes have been studied on reduced TiO$_2$(0 0 1). The conversion of acetylene, methyl acetylene, 2-butyne, *tert*-butyl acetylene, and TMSA is shown in Fig. 10, and the trend in hydrogenation selectivity tracks the conversion of those molecules [5,16]. We have observed previously that molecules with a greater number of acetylenic hydrogens yield greater amounts of hydrogenation products. However, TMSA, which would be expected to exhibit

a hydrogenation selectivity comparable to that of *tert*-butyl acetylene and less than that of acetylene on this basis, gives rise to the greatest hydrogenation selectivity among the five reactants in Fig. 10. This difference likely reflects steric inhibition of TMSA oligomerization, making the hydrogenation channel more competitive.

Earlier work by this group has shown that cyclotrimerization of bulky alkynes is possible [16]. *Tert*-butyl acetylene reacted on the reduced TiO$_2$(0 0 1) surface to form tri-*tert*-butylbenzene at a selectivity approaching 50%. Comparison of the dimer and cyclotrimer selectivities between methyl acetylene and *tert*-butyl acetylene reveals the relative difficulty of inserting the last monomer to complete the cyclotrimer. It is even more difficult to cyclize TMSA, and this is the only reactant examined that exhibits higher selectivity to dimers than to the cyclotrimer. If the reaction intermediates populate the surface in a distribution influenced by steric effects (both in terms of spatial distribution on the surface as well as the mass and structural distribution of TMSA-derived species), metallacycles with the pendant groups separated as far apart as possible might not be able to insert the final monomer. It was not possible to distinguish the 1,2,4 and 1,3,5-isomers of tris-(trimethylsilyl)-benzene in our experiments, and neither compound was commercially available, although both compounds have been characterized. Regioselectivity in solution-phase [2 + 2 + 2] cycloaddition reactions has been attributed to polarization of the alkyne π^* system. Stockis and Hoffmann suggested that the large lobes rest on the terminal acetylenic carbon in TMSA, and that these lobes face each other in the metallacyclopentadiene [17]. Mori et al. demonstrated that the nickelacyclopentadiene formed from TMSA has the trimethylsilyl groups in the first and fourth positions; thus, only the 1,2,4-isomer of the cyclotrimer could be formed. The 1,3-substituted nickelacyclopentadiene was not formed in their experiments. In contrast, Mori et al. showed that nickelacyclopentadienes formed from *tert*-butyl acetylene could convert between 1,4- and 1,3-substituted positions, with equilibrium favoring the 1,4-nickelacyclopentadiene [18]. Thus, the steric hindrance observed for cyclotrimerization on reduced TiO$_2$(0 0 1) surfaces imposed by the much larger trimethylsilyl group is hardly surprising.
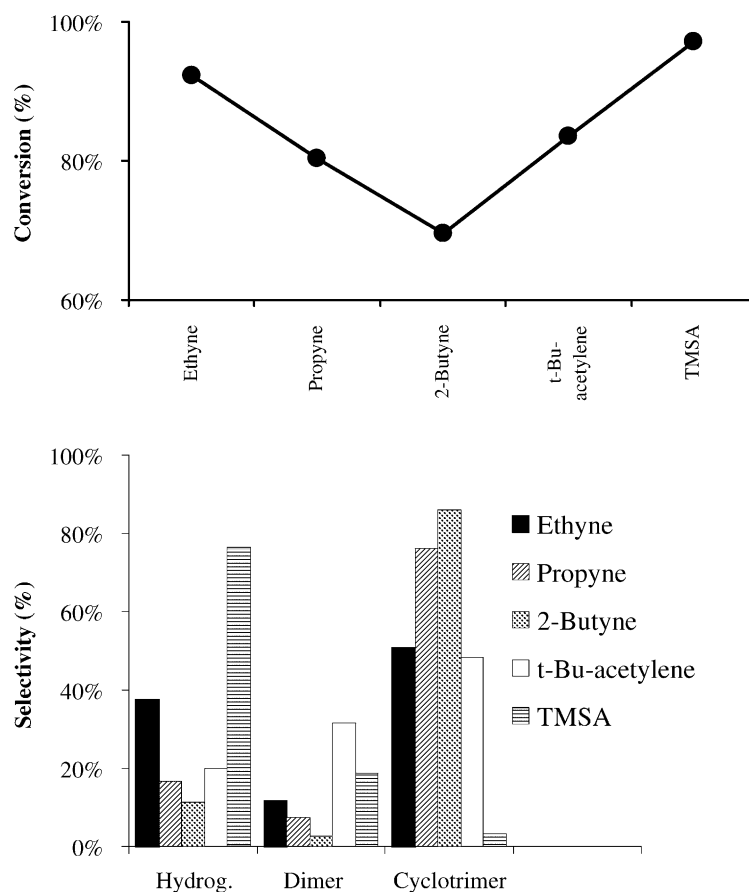
Fig. 10. Product selectivity and reactant conversion for several alkynes on reduced surfaces of $TiO_2(0\,0\,1)$. The decline in cyclotrimer selectivity and the cyclotrimer/dimer ratio with increasing functional group size reveals the effect of steric influences on the carbon–carbon bond forming reaction.
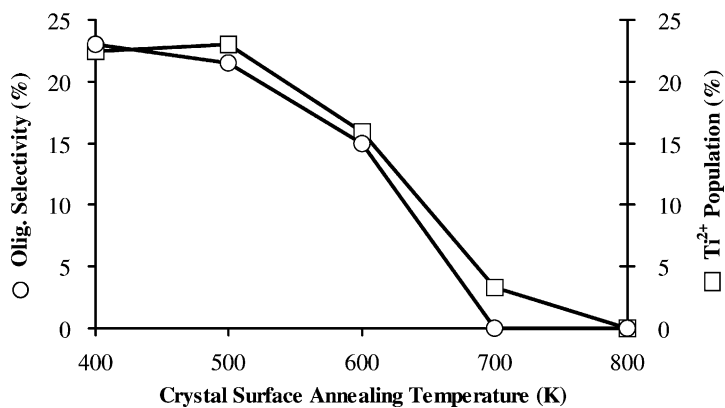

Fig. 11. TMSA oligomerization selectivity as a function of prior annealing temperature of the sputtered $TiO_2(1\,1\,0)$ surface. The selectivity to form oligomeric products is dependent on the population of Ti^{2+} cations at the surface.

5. Conclusions

The oligomerization of trimethylsilyl acetylene on reduced surfaces of $TiO_2(0\,0\,1)$ has been demonstrated. The expected dependence of this reaction on the availability of Ti^{2+} cations, demonstrated in past experiments using smaller alkynes, has been reproduced here. X-ray photoelectron spectroscopy has shown that the oligomeric products are formed on the surface below 220 K, and are the dominant adsorbates present on the surface at that temperature. The primary reaction on both reduced and stoichiometric surfaces of this crystal plane is hydrogenation of TMSA to form trimethylvinylsilane, the monomer olefin, and trimethylsilane, a decomposition product formed by proton transfer. Comparison of the dimer/cyclotrimer selectivity ratio for TMSA with those of smaller alkynes illustrates the difficulty of the cyclization reaction for this monomer. It is likely that an energetic barrier for the insertion of the final monomer molecule determines the preferential formation of dimer over cyclotrimer for the oligomeric products. Steric effects may also influence the formation of the proposed metallacyclopentadiene intermediate.

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