DOI: 10.1002/ejic.200901092

Silicon-Assisted Direct Covalent Grafting on Metal Oxide Surfaces: Synthesis and Characterization of Carboxylate N,N′-Ligands on TiO_2

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Keywords: Titanium oxide / Ligand grafting / Molybdenum / Oxidation

The easy covalent bonding of an OH-bearing molecule onto a metal oxide surface can be done by transesterifying a trimethylsilylated hydroxy function with the surface OH groups. This results in the grafting of the organic molecule directly on the matrix, accompanied by the formation of trimethylsilanol, which can easily be eliminated as volatile hexamethyldisiloxane and water. This was accomplished on a TiO_2 matrix with three carboxylic acids: acetic, isonicotinic, and 2,2′-bipyridyl-4,4′-dicarboxylic acids. The N,N′-immobilized ligand was then used for a dioxidomolybdenum entity and tested as such at room temperature and under atmospheric pressure O_2 oxidation of ethylbenzene. All intermediates and grafted species were fully characterized by ^{13}CMAS NMR spectroscopy, and thermogravimetric and elemental analysis.

Introduction

Numerous solid matrices, essentially silica-based, have been functionalized with organic and organometallic entities, and their use as active sites for sensors,[1] nanoelectronics,[2] and photonic devices, as well as chromatographic materials,[3] is widespread. Various methods exist to insert organic functional groups into these matrices.[4–8] They mostly involve the reaction of organosilanes with the silanol group of the silica matrix.[9] The nature of the resulting material depends heavily on the experimental conditions used during the grafting and parameters such as the temperature, the dilution, or the polarity of the solvent often lead to products having different properties.[10,11] Equally important are titania matrices onto which organic moieties bearing generally carboxylic acid functions have been grafted, almost exclusively by adsorption phenomena, and thoroughly studied by various spectroscopic techniques.[12–17] Among these, many have also been combined with, in particular, ruthenium chromophores and used as efficient photosensitizers.[18–23]

When the grafted material is to be used for catalytic purposes, the bonding to the solid matrix must be truly covalent in nature and not prone to desorption, as it is in the case for simply adsorbed species. Most solid supports in catalysis that are studied are silica-based matrices and involve various silane-binding agents.[24] Among these, molybdenum complexes, reported as active catalysts in oxidation reactions, have been recently anchored on silica surfaces. Dioxidomolybdenum complexes bearing nitrile or bipyridyl ligands were reported, but met with molybdenum leaching problems.[25,26] A slight improvement was obtained with 1,4-diazabutadiene,[27,28] but real progress was made with pyrazoylpyridine ligands, tethered with an amide functionalized spacer.[29] Likewise, oxido-peroxidomolybdenum complexes, well known as epoxidation catalysts, were anchored on mesoporous surfaces by an acetamide spacer bearing a pyrazoylpyridine ligand.[30,31] The system showed no significant leaching and was as active as the corresponding homogeneous catalyst.

All these oxidation reactions were run with alkyl hydroperoxide as the oxidizing agent. Dealing with O_2 as the direct oxygen atom donor is a more arduous problem and real workable catalytic systems are scarce. We have reported, over the years, the synthesis of several complexes bearing oxido, dioxido, μ-oxido, or peroxido ligands and studied, under homogeneous conditions, their properties as oxygen atom transfer agents with various O-donors.[32–40] Some aroused high interest, specially when found to be active with O_2 as the oxygen atom donor. Recently, we have significantly optimized the catalytic behavior of these systems by anchoring them covalently on the semiconductor solid matrix, anastase TiO_2.[41,42] The improvement was attributed to the site isolation of the metallic centers, to avoid any undesired oligomerization and deactivation, but also to the role of the photogenerated flux through TiO_2 on the O-atom transfer process as well as the activation of dioxygen by the reduced molybdenum species in the catalytic cycle.

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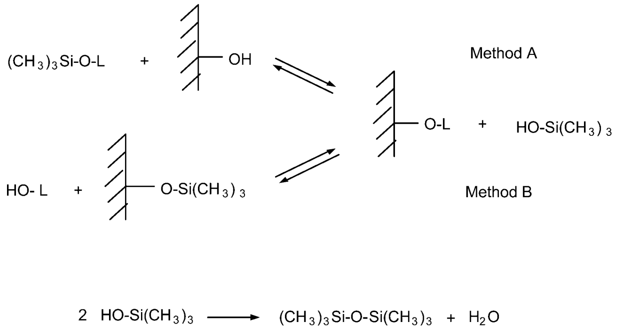
When dealing with O_2 as the oxygen atom donor, the charge transfer from TiO_2 to the molybdenum coordination sphere is most efficient when the tethering linkage is as short as possible. We chose the spacer 4,4′-dicarboxyl-2,2′-bipyridine bonded to the dioxidomolybdenum entity and *directly anchored covalently* onto the TiO_2 surface through the carboxylic function. The synthetic route to achieve the covalent anchoring of the molybdenum complex on the TiO_2 matrix was a multistep procedure.[41,42] It was somewhat difficult to carry out and would probably be inadequate if applied to larger quantities.

We report here an original approach for a new synthetic route to anchor an organic molecule bearing a carboxylic acid function directly and covalently on TiO_2. It is a much simpler, nearly one-pot, procedure based on the cross-transesterification of either the trimethylsilyl carboxylic ester with the titanol function present on the surface of the oxide or the reaction of a trimethyl silylated TiO_2 matrix with the free carboxylic acid. This results in the covalent bonding of the carboxylate entity on the titanium oxide surface accompanied by the formation of trimethyl silanol, which can be easily eliminated from the reaction medium as low boiling hexamethyldisiloxane and water, shifting, thus, the transesterification equilibrium towards the grafted carboxylate species. This new synthetic strategy was tested with acetic and isonicotinic acids as models and then with 2,2′-bipyridyl-4,4′-dicarboxylic acid and the parent dioxidomolybdenum complex.

Results and Discussion

Most inorganic oxides used as support for the immobilization of catalytically active sites present hydroxy groups on their surface and it is through these functions that the introduction of ligand groups bonded or not to transition metals is obtained.[9] The most common are silica surfaces and the anchoring is attained by treating the desired ligand bearing an amino, halo, or, most frequently, alkoxy silane with the surface silanol groups.[10,11] These multistep reaction procedures are often performed in acid-catalyzed aqueous medium, allowing a high percentage of incorporation (coating), but also under noncatalyzed anhydrous conditions, which necessitate a longer reaction time. This second mode yields a lower level of incorporation (grafting) but, on the other hand, a better defined bonding.[11] In all cases, however, the resulting hybrid material unavoidably comprises the inorganic oxide support and the silane moiety bearing the ligand or organic group.

The novel approach we present allows, in a nearly one-pot procedure, the *direct covalent bonding* of a spacer ligand onto the oxide surface, with a high degree of incorporation and without any leaching-prone silane link. It consists of treating the trimethylsilylated hydroxy function of the desired ligand with the OH groups present on the inorganic oxide surface (Method A). This results in a transesterification yielding, on one hand, the bound ligand on the oxide and, on the other, trimethylsilanol, which irreversibly gives hexamethyldisiloxane and water, easily eliminated in vacuo, thus shifting the equilibrium to the right (Scheme 1). Alternatively, one can trimethylsilylate the hydroxy functions on the oxide surface and treat them with the HO-bearing organic entity (Method B) to attain, by an analogous route, the same ligand-bound surface (Scheme 1). It is noteworthy that the material obtained by these routes is different in nature from a simply adsorbed molecule because, once the trimethylsilanol is eliminated, corresponding to the loss of one oxygen and one hydrogen atom per titanol site, no desorption is thereafter possible. This is in contrast to a chemisorbed species obtained, for example for acids, by a dissociative process wherein the carboxylate ion bonds to titanium and the proton bonds to a bridging oxygen atom.[16,43]



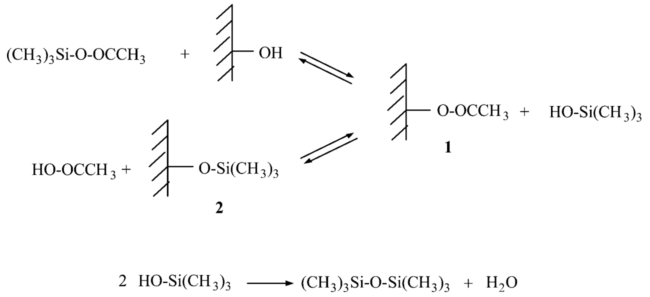
Scheme 1.

This new method was tried and realized on a titanium oxide surface (Degussa P-25) with three different carboxylic acids: acetic and isonicotinic acids as models and 2,2′-bipyridyl-4,4′-dicarboxylic acid as an immobilized ligand for dioxidomolybdenum complexes.

Trimethylsilylation of carboxylic acids can be accomplished with various trimethylsilyl blocking agents such as chlorotrimethyl-,[44] cyano-,[45] isopropenoxy-,[46] or allylsilanes[47]. The choice for the present study was bis(trimethylsilyl)urea,[48] based on stability, toxicity, and reactivity factors. The trimethylsilylation of the titanium oxide surface (Degussa P-25) was realized with hexamethyldisilazane.[49]

Acetic Acid

Trimethylsilyl acetate, commercially available, was directly treated in benzene with a thoroughly dried titanium oxide sample (Degussa P-25). An excess of silyl ester was used, as the unreacted amount could easily be washed away when the reaction was completed. To prove the tethered character of the acetate moiety in the resulting solid (**1**) (0.44 mmol/g) (Scheme 2), ^{13}CMAS NMR spectroscopy is the method of choice. As shown in part b of Figure 1, the resonance at 179.7 ppm assigned to the C=O anchored function is significantly different from the trimethylsilyl acetate (δ = 170.5 ppm). Apart from a signal at δ = 10 ppm, assigned to residual trimethylsilyl acetate, the spectrum (Figure 1, b) indicates that the reaction proceeded nearly to completion. The surface-bound acetate group was estimated at a loading of 0.44 mmol/g, based on elemental analysis and corroborated by thermal gravimetric analysis (0.43 mmol/g).



Scheme 2.

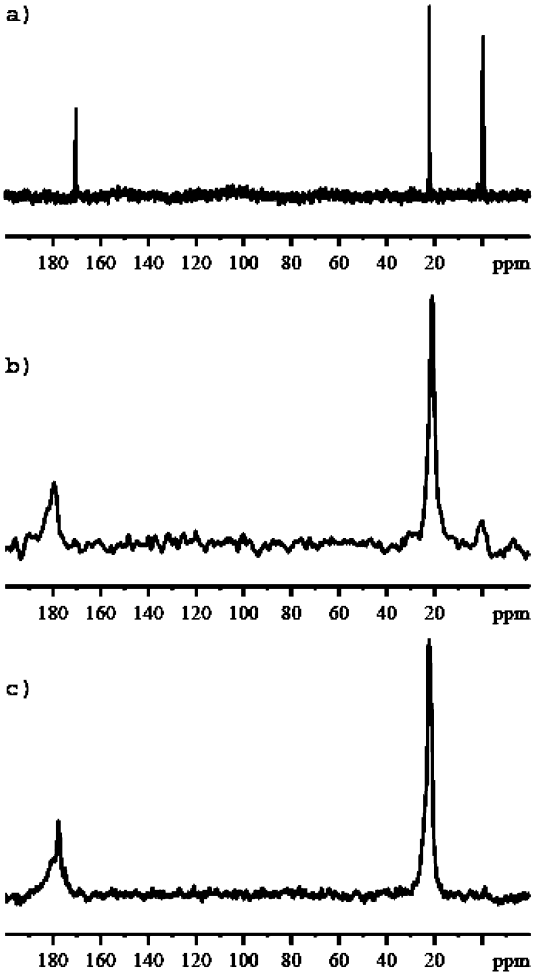


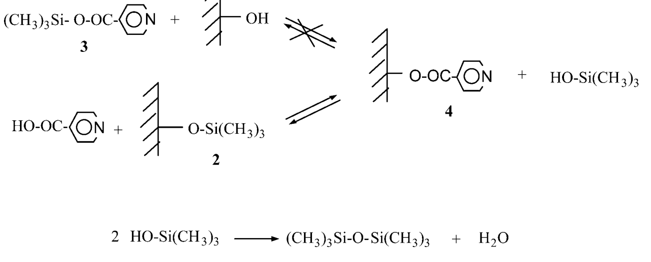
Figure 1. ^{13}CMAS NMR spectrum of $(CH_3)_3Si–OOCCH_3$ (a) and **1** (b) by Method A, and **1** (c) by Method B. Signal at 10 ppm in (b) is assigned to residual trimethylsilyl acetate.

The covalent grafting of the acetate function on the titanium oxide surface was also accomplished by Method B. The titanol groups, estimated at 0.5 mmol/g of oxide (Degussa P-25), were silylated with an excess of hexamethyldisilazane and treated directly with glacial acetic acid. The ^{13}CMAS NMR analysis (Figure 1, c) indicated clearly that the transesterification had occurred (0.22 mmol/g), namely by the total absence, upon workup, of any Si-CH$_3$ signal. It indicated, however, a slight difference with the sample obtained by Method A. This could be rationalized in terms of a difference in aggregation of the grafted groups because of the two distinct reaction conditions. Such difference has previously been observed, for example, in the degree of site isolation, simply by varying the polarity of the reaction medium.[11,50] The loading was estimated by elemental and thermal gravimetric analyses and corresponds to the extent of trimethylsilylation of **2**, which in turn depends on the degree of moisture present during the silylation of the TiO$_2$ matrix.

Isonicotinic Acid

The silylation of isonicotinic acid was performed with bis(trimethylsilyl)urea and it was then isolated. However, when treated with the titanium oxide (Method A), only a small fraction could be immobilized covalently on the surface, the rest being recovered as the free acid simply by washing the resulting reaction mixture. This is plausibly due to the extreme proneness to hydrolysis of the isonicotinic silyl ester with the water that arises from the dehydration of the trimethylsilanol formed during the transesterification step. Method A was thus abandoned, in this case, as a workable synthetic route.

The grafting of the isonicotinate function on the titanium oxide surface, on the other hand, was easily obtained by Method B (Scheme 3). Elimination under vacuum of hexamethyldisiloxane and water from the reaction medium shifted the equilibrium and yielded nearly pure hybrid material. It was shown by ^{13}CMAS NMR analysis to consist of a truly tethered carboxylate function significantly different from a simply absorbed free acid obtained by mechanically mixing isonicotinic acid and TiO$_2$ as shown in Figure 2. This is indeed indicated by the very different δ values (165.1 vs. 167.8, Figure 2, c) and further corroborated by the broadness of the signals in **4**, which strongly supports the tethered character because of its reduced mobility. The absence of any Si-CH$_3$ signal confirmed this. Its stability underlined, furthermore, its resistance to hydrolysis compared to its silyl analog. The extent of covalent loading on the surface was estimated by elemental (0.31 mmol/g) and thermogravimetric (0.23 mmol/g) analyses and, as in the case of acetic acid, corresponded to the extent of trimethylsilylation of the TiO$_2$ used.



Scheme 3.

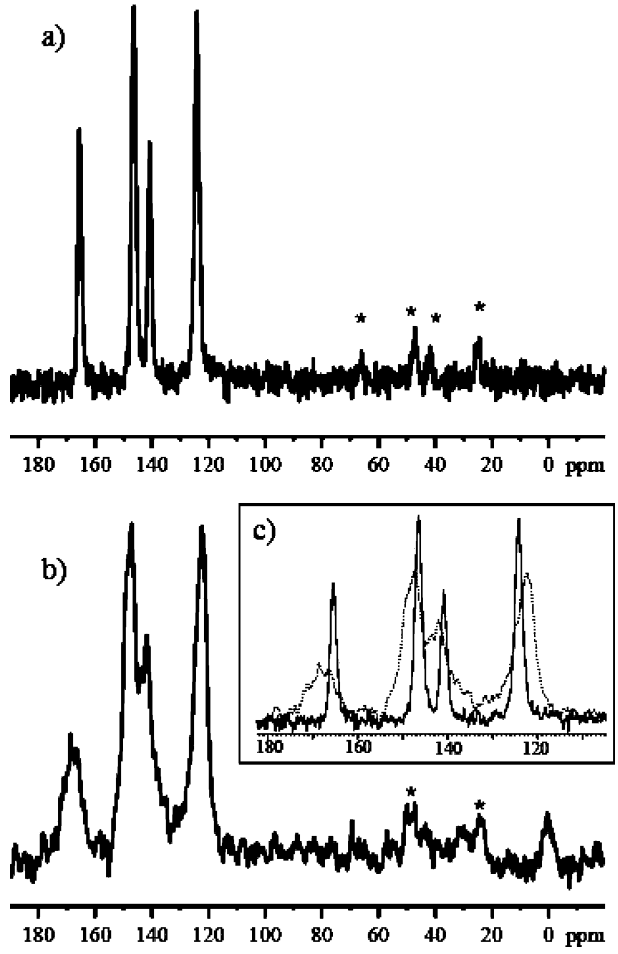


Figure 2. ^{13}CMAS NMR spectrum of solid mixture of isonicotinic acid and TiO_2 (a) and **4** (b), and superimposition of a (—) and b (····) (c). * Spinning side bands.

2,2′-Bipyridyl-4,4′-dicarboxylic Acid

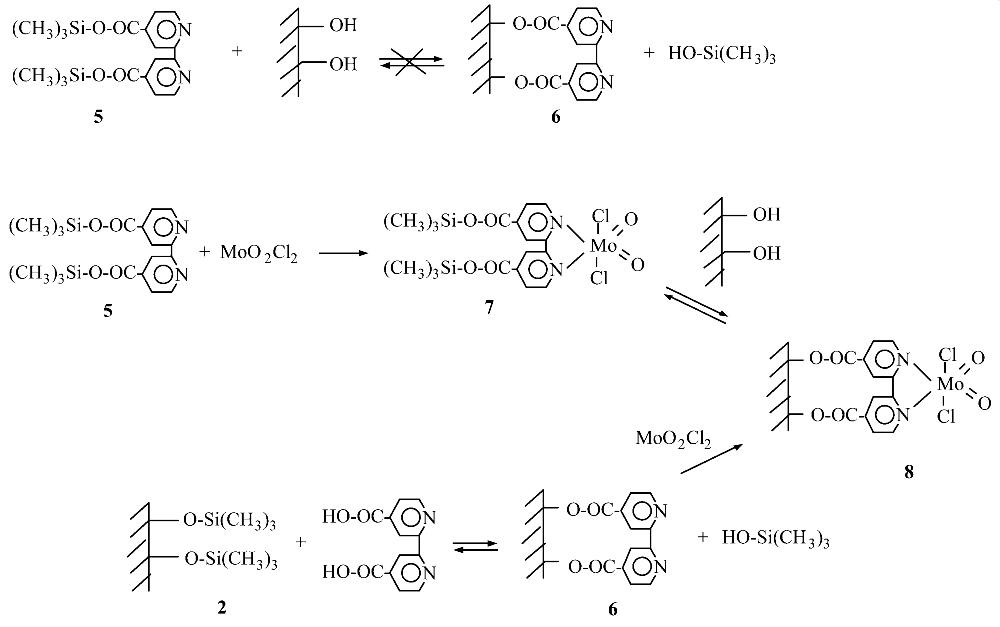
Double silylation was performed with bis(trimethylsilyl)urea and it was isolated. However, as in the case of isonicotinic acid, the transesterification with the titanol groups on the oxide surface failed, partially because of the prompt hydrolysis of the silyl ester. This difficulty with Method A was circumvented, however, by complexing, at first, the disilylated bipyridyl diacid with a dioxidomolybdenum entity, modifying thus the electronic character of the carboxylate function and making it less prone to hydrolysis. Indeed, when the complex dichlorodioxido(4,4′-trimethylsilylcarboxy-2,2′-bipyridyl)molybdenum (**7**) was treated with titanium oxide, a clean covalent grafting through the carboxylate functions was obtained (Scheme 4). Its ^{13}CMAS NMR analysis (Figure 3, c) was shown to be significantly different from the spectrum of **7** (Figure 3, b). All δ values are different but, as expected, this is more pronounced for the carbonyl function (161.5 for **7** vs. 165.0 for **8**). The broadness of the signals for **8** compared to **7** is, furthermore, strong evidence of its tethered character. In addition, the absence of any Si-CH_3 signal corroborated the grafting of the carboxylate entity. The surface-bound complex was estimated at a loading of 0.229 mmol/g by elemental analysis and 0.234 mmol/g by TGA. This same grafted complex, obtained by a multistep procedure, has previously been reported and fully characterized by UV-diffuse reflectance, and IR-acoustic as well as solid-state ^{15}N NMR spectroscopy.[41,42]

The same anchored complex could also be obtained by Method B. As for the isonicotinic acid, an excess of free diacid was treated with trimethylsilylated titanium oxide. The ^{13}CMAS NMR showed (Figure 3, e), as expected, the presence of both the immobilized (**6**) and the free ligand. The spectrum shown in Figure 3 (e) clearly illustrates the distinction between the tethered and the simply absorbed species. This is indicated not only in the difference of the δ values but, more importantly, in the broadness of the signals of the grafted material. Treating this mixture with MoO_2Cl_2 resulted in the exclusive complexation of the anchored ligand. This is in good accordance with the previous observation[42] that the free bipyridyl diacid is a very poor ligand because of the strong electron-withdrawing character of the –COOH function *para* to the heteroatom. The ^{13}CMAS NMR analysis (Figure 3, f) of the final (one-pot) product clearly indicated the covalent anchoring of the bipyridyl ligand complexed to the MoO_2Cl_2 moiety. The extent of loading (0.11 mmol/g) in this case is directly dependent on the percentage of trimethylsilylation of the TiO_2 matrix. It should be noted that when the diacid is simply adsorbed on titania, following the reported procedure,[16] the material obtained does not react with MoO_2Cl_2 to give **8**, emphasizing the different nature of **6** and the adsorbed diacid.

The reaction routes shown in Scheme 4 indicate a vicinal grafting pattern of the bipyridyl carboxylate function. Without any further evidence, this should only be considered as a simplified drawing. Although a vicinal addition mode is most plausible with Method A, a different anchoring pattern with Method B remains possible, leading to a slightly different mode of aggregation complex **8**.

Catalytic Oxidation of Ethylbenzene with O_2

Ethylbenzene has been shown previously to be selectively oxidized with O_2, at room temperature and atmospheric pressure in the presence of the catalytic system[42] analogous to **8**. It was interesting to check if the various synthetic routes reported in the present study for such a system had an effect on its reactivity, as the nature of the grafting mode could plausibly lead to species bearing different bonding. The protocol used was analogous to the one reported previously,[42] namely, by following the formation of acetophenone with time. Alternatively, under N_2 and visible light, a stoichiometric O-transfer occurs from the dioxidomolybdenum(VI) complex to the substrate, followed by a period under O_2 in the dark during which the reduced Mo^{IV} oxido species is reoxidized. The sequence can be repeated at will.



$$2\ HO\text{-}Si(CH_3)_3 \longrightarrow (CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3 + H_2O$$

Scheme 4.

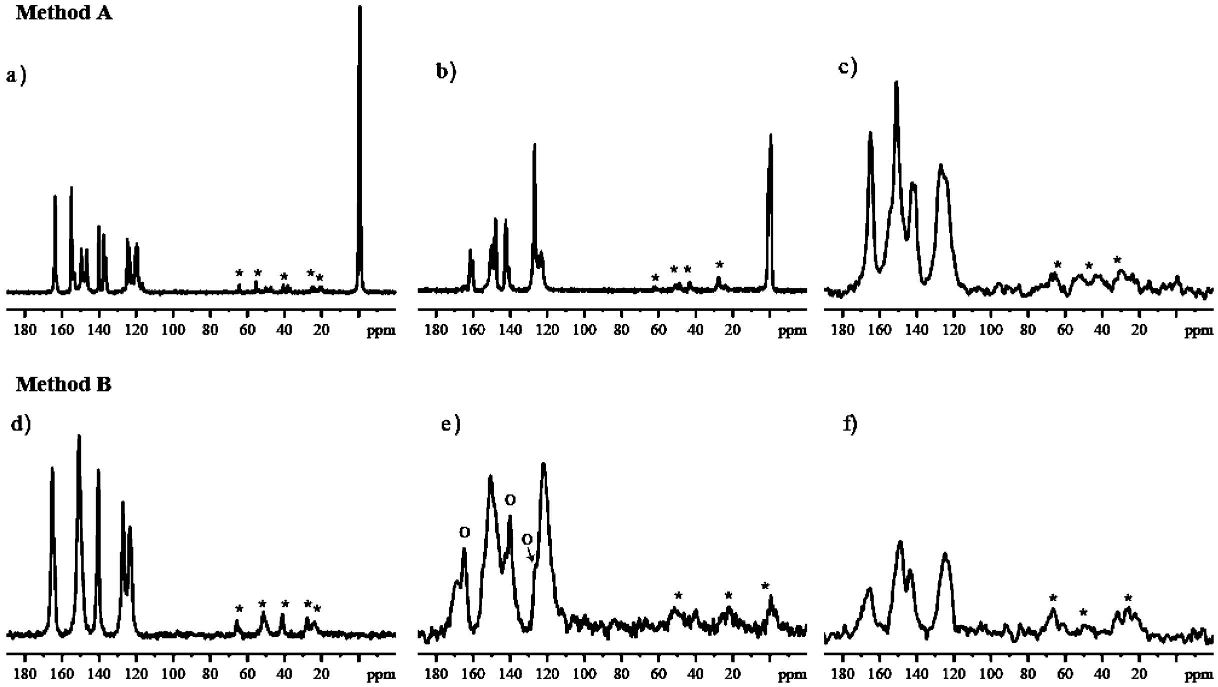


Figure 3. ^{13}CMAS NMR spectra of **5** (a), **7** (b), and **8** (c) by Method A, and 2,2′-bipyridyl-4,4′-dicarboxylic acid (d), **6** (e), and **8** (f) by Method B. * Spinning side bands, ° residual free diacid.

The results obtained with the grafted complex (**8**) prepared by methods A and B are depicted in Figure 4 and compared with the unbound analogous homogeneous system constituted of dibromodioxido(4,4′-dimethoxycarbonyl-2,2′-bipyridyl)molybdenum (**9**)[41,51] in a slurry of pure TiO_2. Even though the metal loading is different for complex **8**, obtained by Method A (0.23 mmol/g) and Method B (0.11 mmol/g), the reaction pattern is nearly the same when

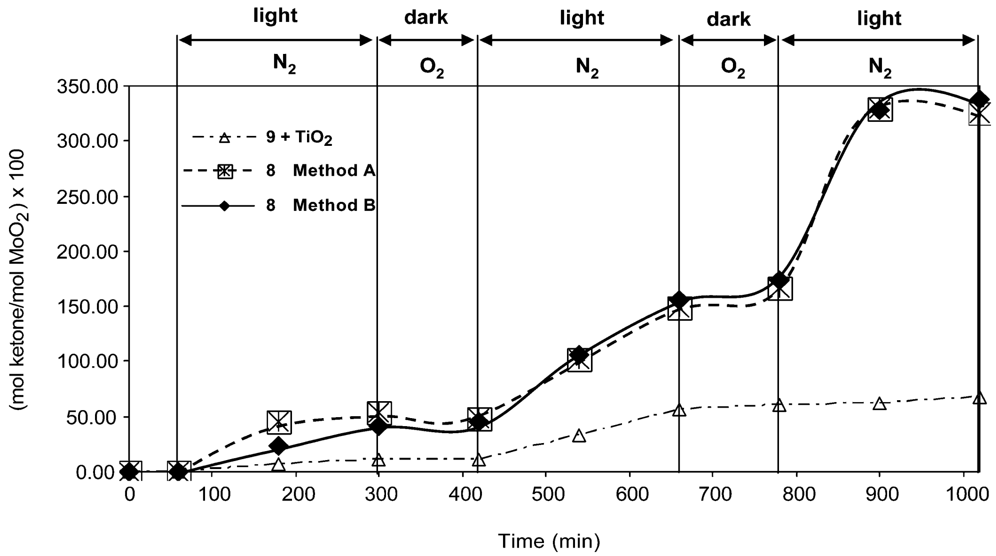
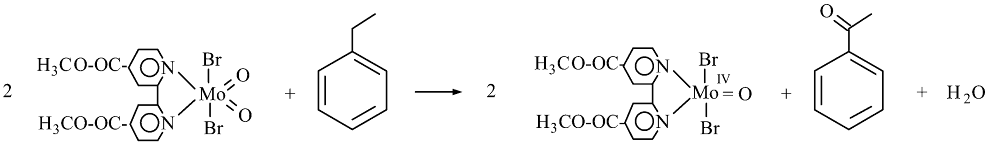


Figure 4. Ethylbenzene oxidation. Time evolution of [mol acetophenone]/[mol MoO_2] as a function of time.



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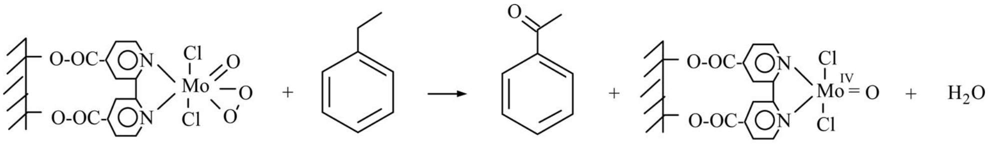
Scheme 5.



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Scheme 6.

equimolar concentrations of grafted complex are used, in contrast to the unbound homogeneous system, which is drastically different.

The slow rate of acetophenone formation with complex **9** indicates the successive transfer of two O atoms from two moles of **9** to give, after 11 h, a yield of slightly over the expected 50% (Scheme 5). The curve clearly indicates that the system becomes, thereafter, inactive and the O-transfer stops once the $Mo(O)_2$ entity is consumed.

On the other hand, the grafted system (**8**), obtained either by Method A or B, follows a reaction pattern analogous to the one reported earlier.[30] Under N_2 and visible light the first 50% of acetophenone is formed within one hour. The resulting reduced Mo^{IV} species is then reoxidized in the dark with O_2 to give a oxido-peroxidomolybdenum(VI) entity (**10**) capable of transferring two oxygen atoms to the substrate under N_2 and visible light. The sequence can then be repeated by reoxidizing the reduced Mo^{IV} species with dioxygen (Scheme 6).

These results strongly imply the covalent bonded character of the molybdenum entity onto the TiO_2 surface obtained by either Method A or B. Furthermore, the similarity in the reaction pathway indicates that the probable differences in the anchoring mode on the TiO_2 matrix have little effect on its reactivity. The main distinction observed between the species obtained by the two synthetic routes resides in the percentage of metallic centers bound to the surface.

Conclusions

The direct covalent bonding of a carboxylate function onto a TiO_2 surface has been achieved by a new, nearly one-pot, synthetic route involving the transesterification of a trimethylsilyl ester and the OH group present on the surface of the matrix (Method A) or, alternatively, a trimethylsilylated TiO_2 and a carboxylic acid (Method B). Both pathways are accompanied by the formation of trimethylsilanol, which is easily eliminated from the medium as low boiling hexamethyldisiloxane and water. The reaction was tested with acetic and isonicotinic acids and then extended to 2,2′-bipyridyl-4,4′-dicarboxylic acid bonded to a dioxidomolybdenum entity. The tethered molybdenum complexes obtained by both methods were fully characterized and then tested in the O_2 oxidation of ethylbenzene under visible light, at room temperature and atmospheric pressure. The results indicated that the nature of the two anchored species obtained by the different synthetic routes had no major effect on their reactivity as an oxygen atom transfer agent. This new approach to covalently and directly anchoring OH-bearing molecules on solid matrices is presently being extended to other systems. From a practical point of view, the present work shows a higher metal loading with Method A, but Method B could be considered easier to apply, especially if the trimethylsilylation of titania is optimized.

Experimental Section

General: All materials were of commercial grade and were used without further purification unless otherwise noted. All solvents were thoroughly degassed prior to use. Acetonitrile was distilled and kept under argon. Titanium oxide (Degussa P-25) with 50 m^2/g specific area and crystalline structure of 80% anastase and 20% rutile was dehydrated at 60 °C and 5×10^{-4} mbar for 48 h prior to use. IR (KBr) were recorded with a Perkin–Elmer 1720XFT. ^1H and ^{13}C NMR were performed with Bruker Avance 200 and 400 spectrometers. All solid-state CPMAS NMR spectra were obtained with a Bruker Avance-400 MHz NMR spectrometer operating at a ^{13}C resonance frequency of 101.6 MHz. The ^{13}C experiments were performed with a commercial Bruker double-bearing probe with zirconium dioxide rotors of 4-mm outer diameter. The CP technique[52] was applied during Magic Angle Spinning (MAS) of the rotor at 10 kHz. A ramped ^1H-pulse starting at 100% power and decreasing until 50% was used during contact time in order to circumvent Hartmann–Hahn mismatches.[53,54] The contact time was 2 ms. To obtain a good signal-to-noise ratio in ^{13}C CPMAS experiments, 2048 scans were accumulated using a delay of 2 s. The ^{13}C chemical shifts were referenced to tetramethylsilane and calibrated with glycine carbonyl signal, set at δ = 176.5 ppm. The thermogravimetric analysis was performed using a Micromeritics piece of equipment with a thermogravimetric analyzer TGA 2950 Hi-Re. The team was operated by a heating ramp of 10.00 °C/min in a range between 30.0 and 900 °C with a sensitivity and high resolution of 8.0 °C. Gas chromatography (GC) analysis of the photooxidation products was performed with a HP-6890 equipped with a flame ionization detector and HP5 column (30 m × 0.32 mm × 0.25 µm). Toluene was used as internal standard.

Reaction of Trimethylsilyl Acetate with TiO_2: Trimethylsilyl acetate (0.150 mL, 0.13 g, 1 mmol) was added to a benzene suspension (40 mL) containing thoroughly dried TiO_2 (1.0 g, 60 °C, 10^{-5} mbar, 24 h; Degussa P-25, estimated 0.5 mmol of –OH/g). The mixture was slowly stirred at 25 °C for 24 h and filtered. The resulting solid (**1**) was thoroughly washed with benzene (2 × 25 mL) and dried under vacuum. ^{13}C NMR/CPMAS: δ = 179.7, 20.9 ppm. Total absence of Si-CH_3 signal (–0.5 ppm). Loading: 0.432 mmol/g of TiO_2 by TGA; 0.445 mmol/g of TiO_2 by elemental analysis.

Reaction of Acetic Acid with Trimethylsilylated TiO_2: Glacial acetic acid (0.360 mL, 0.38 g, 6.3 mmol) was added to a benzene suspension (40 mL) containing freshly prepared trimethylsilylated TiO_2 (**2**), obtained from TiO_2 (1 g; Degussa P-25), and the mixture slowly stirred at room temperature for 24 h. The resulting mixture was filtered and the solid (**1**) thoroughly washed with benzene (3 × 25 mL) and dried under vacuum. ^{13}C NMR/CPMAS: δ = 179.8, 22.1 ppm. Total absence of Si-CH_3 signal (–1.4 ppm). Elemental and gravimetric analyses indicate a percentage of acetate function in **1** corresponding to the degree of silylation in **2**: loading is 0.220 mmol/g of TiO_2 from **2** containing 0.240 mmol of $Si(CH_3)_3$/g.

Trimethylsilylation of TiO_2 (Degussa P-25) with Hexamethyldisilazane: Hexamethyl disilazane (0.5 mL, 2.4 mmol) was added to a benzene suspension (40 mL) containing thoroughly dried (60 °C, 10^{-5} mbar, 24 h) TiO_2 (1 g, Degussa P-25, estimated 0.5 mmol of –OH/g). The suspension was stirred at room temperature for 24 h and the resulting solid (**2**) was filtered, washed thoroughly with benzene (2 × 25 mL), and dried under vacuum. ^{13}C NMR/CPMAS: δ = –1.4 ppm. The extent of trimethylsilylation varies from 0.25 to 0.35 mmol/g depending on the degree of moisture in the reaction medium.

Trimethylsilylation of Isonicotinic Acid: Bis(trimethylsilyl)urea (816 mg, 4 mmol) was added to a CH_2Cl_2 solution (40 mL) containing isonicotinic acid (984 mg, 8 mmol) and the mixture was refluxed for 6 h. The resulting suspension was filtered and the filtrate evaporated cautiously in vacuo (<25 °C) to yield a white solid (**3**) (960 mg, 67%). IR (KBr): $\tilde{\nu}$ = 1717 (C=O), 857 (Si-CH_3) cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2, 23 °C): δ = 8.74 (d, 2 H, CH, arom.), 7.81 (d, 2 H, CH, arom.), 0.39 (s, 9 H, $SiMe_3$) ppm.

Reaction of Isonicotinic Acid with Trimethylsilylated TiO_2: Isonicotinic acid (45 mg, 0.365 mmol) was added to a benzene suspension (40 mL) containing freshly prepared trimethylsilylated TiO_2 (**2**), obtained from TiO_2 (1 g, Degussa P-25). The mixture was slowly stirred at 25 °C for 24 h and the solid (**4**) filtered, washed thoroughly with benzene (3 × 25 mL), and dried under vacuum. ^{13}C NMR/CPMAS (400 MHz, solid, 23 °C): δ = 168.6 (s, 1 C, COO), 147.3 (s, 2 C, CH, arom.), 149.9 (s, 1 C, arom.), 122.4 (s, 2 C, CH, arom.) ppm. Total absence of Si-CH_3 signal (–1.4 ppm). For a solid mixture of isonicotinic acid and TiO_2: δ = 165.4 (s, 1 C, COO), 146.4 (s, 2 C, CH, arom.), 143.7 (s, 1 C, C, arom.), 124.0 (s, 2 C, CH, arom.) ppm. The percentage of isonicotinate in **4** corresponds to the degree of silylation in **2**. Loading: from a sample of **2** containing 0.35 mmol of $Si(CH_3)_3$/g: 0.233 mmol/g of TiO_2 by TGA, 0.31 mmol/g of TiO_2 by elemental analysis.

Trimethylsilylation of 2,2′-Bipyridyl-4,4′-dicarboxylic Acid: Bis(trimethylsilyl)urea (0.102 g, 0.5 mmol) was added to a benzene suspension (40 mL) containing 2,2′-bipyridyl-4,4′-dicarboxylic acid (0.120 g, 0.5 mmol). The suspension was heated to reflux for 4 h, cooled to room temperature, and filtered. The filtrate was evaporated to yield the product **5** as a white solid. IR (KBr): $\tilde{\nu}$ = 1702 (C=O), 850 (Si–CH_3) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 23 °C): δ = 8.91 (dd, 2 H, CH), 7.89 (dd, 2 H, CH), 7.30 (d, 2 H, CH), 0.44 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR (200 MHz, 23 °C): δ = 156.7 (s, 2 COO), 152.9 (s, 2 C), 150.1 (s, 2CH), 128.4 (s, 2 C), 123.4 (s, 2CH), 121.1 (s, 2CH), 0.14 (s, 6 C, $SiMe_3$) ppm. ^{13}C NMR/CPMAS (400 MHz, solid, 23 °C): δ = 163.7 (s, 2 COO), 154.9 (s, 2 C), 149.6 and 137.6 (s, 2 CH), 140.1 and 137.6 (s, 2 C), 124.8 and 123.6 (2CH), 120.4 and 119.6 (s, 2CH), 0.2 and 0.5 (s, 6 C, $SiMe_3$) ppm.

Reaction of 2,2′-Bipyridyl-4,4′-dicarboxylic Acid with Trimethylsilylated TiO_2: 2,2′-Bipyridyl-4,4′-dicarboxylic acid (122 mg, 0.5 mmol, 100% excess) was added to a benzene suspension

(50 mL) containing freshly prepared trimethylsilylated TiO_2 (**2**), obtained from TiO_2 (1 g, Degussa P-25). The mixture was stirred for 72 h at room temperature and the resulting mixture was filtered. The solid was thoroughly washed with benzene (3 × 25 min) (**6**). ^{13}C NMR/CPMAS (400 MHz, solid, 23 °C): δ = 168.4 (s, 2COO), 150.7 (s, 2 C) and (s, 2 CH), 140.0 (s, 2 C), 122.1 (s, 2 CH) and (s, 2 CH) ppm. Peaks corresponding to free acid are also observed [δ = 164.7 (s, 2 COO), 140.0 (s, 2 C), 126.4 (s, 2 CH)]. Total absence of $Si-CH_3$ signals (–1.4 ppm).

Dichlorodioxido(4,4′-trimethylsilylcarboxy-2,2′-bipyridyl)molybdenum (7): A benzene solution (40 mL) containing 4,4′-trimethylsilylcarboxy-2,2′-bipyridine (194 mg, 0.5 mmol) (**5**) was added to a benzene suspension (20 mL) containing MoO_2Cl_2 (99.4 mg, 0.5 mmol). The mixture was stirred for 4 h at room temperature resulting in a clear solution. Evaporation of the solvent yielded a white solid (**7**). IR (KBr): $\tilde{\nu}$ = 1705 (C=O), 940, 915 (Mo=O), 850 ($Si–CH_3$) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 23 °C): δ = 9.72 (d d, 2 H, CH), 8.88 (d, 2 H, CH), 8.27 (dd, 2 H, CH), 0.44 (s, 18 H, $SiMe_3$) ppm. ^{13}C NMR (200 MHz, $CDCl_3$, 23 °C): δ = 153.0 (s, 2COO), 150.1 (s, 2 C), 143.4 (s, 2 C), 128 4 (s, 2CH), 127.1 (s, 2CH), 122.9 (s, 2CH), –0.21 (s, 6 CH_3) ppm. ^{13}C NMR/CPMAS (400 MHz, solid, 23 °C): δ = 161.5 (s, 1COOSi), 160.0 (s, 1COOSi), 149.7 (s, 2 C), 148.1 (s, 2CH), 142.4 (s, 2 C), 126.8 (s, 2CH), 123.4 (s, 2CH), 0.2 (s, $3SiCH_3$), 0.5 (s, $3SiCH_3$) ppm.

Reaction of Dichlorodioxido(4,4′-trimethylsilylcarboxy-2,2′-bipyridyl)molybdenum (7) with TiO_2: A benzene solution (50 mL) containing dichlorodioxido(4,4′-trimethylsilylcarboxy-2,2′-bipyridyl)-molybdenum (**7**) (294 mg (0.5 mmol) was added to thoroughly dried (60 °C, 10^{-5} mbar, 24 h) TiO_2 (1 g, Degussa P-25, estimated 0.5 mmol of –OH/g). The suspension was slowly stirred at 25 °C for 12 h, filtered, washed thoroughly with benzene (2 × 30 mL), and dried under vacuum (**8**). ^{13}C NMR/CPMAS (400 MHz, solid, 23 °C): δ = 165.0 (s, 2COO), 148.9 (s, 2C + 2CH), 143.7 (s, 2 C), 124.3 (s, 4CH) ppm. Loading: 0.234 mmol/g of TiO_2 by TGA, 0.229 mmol/g of TiO_2 by elemental analysis.

Reaction of Anchored 2,2′-Bipyridine-4,4′-dicarboxylate on TiO_2 (6) with MoO_2Cl_2: A benzene (30 mL) suspension containing MoO_2Cl_2 (0.10 g, 0.5 mmol) was added under inert atmosphere to a benzene suspension (40 mL) containing freshly prepared 2,2′-bipyridine-4,4′-dicarboxylate anchored on TiO_2 (**6**), obtained from silylated TiO_2 (1 g). The mixture was stirred at room temperature for 72 h. The resulting yellow solid was filtered, washed with THF (2 × 25 mL), and dried under vacuum (**8**). ^{13}C NMR (400 MHz, solid, 23 °C): δ = 165.0 (s, 2COO), 150.7 (s, 2C + 2CH), 142.7 (s, 2 C), 125.2 (s, 2CH) ppm. No signals corresponding to free acid were detected. Loading: from a sample of **2** containing 0.25 mmol of $Si(CH_3)_3$/g: 0.100 mmol/g of TiO_2 by TGA, 0.118 mmol/g of TiO_2 by elemental analysis.

Ethylbenzene Photo-Oxidation: The photocatalytic oxidation of ethylbenzene was carried out using a 10-mL batch microreactor (Ace-Glass model T-121m) with immersion lamp (Phenix, 220 V). In a typical experiment, a 0.081 M solution of ethylbenzene in CH_3CN was thoroughly deoxygenated by bubbling N_2 gas for several hours at 5 °C before the addition of 0.013 g of either MoO_2/TiO_2 (**8**), a "mechanical" mixture of **9**, or TiO_2 in the same proportion as **8**. In all cases the mixture was kept in the dark and under nitrogen for 1 h before visible light was turned on and kept for 4 h. Nitrogen was then replaced by O_2 in the dark. After a period of 2 h the mixture was rendered, again, O_2-free by bubbling N_2 before the light was turned back on. The sequence was repeated at will.

Acknowledgments

Part of this work was performed under the auspices of a BOMPLAN program financed by the French Embassy in Colombia (N. J. C.) The authors are also grateful to Prof. Christian Roussel for fruitful discussions and CHIRBASE for financial support.

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Received: November 10, 2009