Visible Light Driven V-Doped TiO 2 Photocatalyst and Its Photooxidation of Ethanol

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Visible Light Driven V-Doped TiO₂ Photocatalyst and Its Photooxidation of Ethanol

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A vanadium-doped, supported TiO₂ photocatalyst is presented which is quite active using visible (396−450 nm) light. The oxidation of ethanol over this catalyst was studied using ^{13}C solid-state NMR methods that demonstrated that this catalyst photooxidizes ethanol to produce mostly carbon dioxide with small amounts of acetaldehyde, formic acid, and carbon monoxide under visible irradiation. Under UV irradiation, the catalyst has comparable activity and product distribution as a similarly prepared TiO₂ thin-film monolayer catalyst.

Introduction

Because of the pressing need to control and prevent a variety of environmental pollutants, much interest has been paid to photocatalytic methods because they provide a promising strategy for the removal of such contaminants. TiO₂ is known to be one of the most effective photocatalysts for the degradation of organic pollutants, and its photocatalytic behavior has been studied extensively.[1−4] To initiate such reactions, the catalyst surface is irradiated with light of sufficient energy to span the semiconductor's band gap. Electron−hole pairs are subsequently generated that may initiate redox reactions at the surface. Because of the size of its band gap, however, TiO₂ is effective only under ultraviolet irradiation (λ < 380 nm). Because sunlight is comprised of less than 2% ultraviolet light, expensive light sources must often be employed to activate TiO₂ for these reactions to occur. It is, therefore, of great interest to find ways to extend the wavelength range of TiO₂ into the visible region where less expensive light sources exist.

A number of research groups have approached this problem by doping TiO₂ with different transition metal ions in the attempt to create a batho-chromic shift of the band gap energy. For example, Borgarello et al. studied TiO₂ particles doped with Cr^{3+} followed by platination and found that this catalyst could afford water cleavage under visible irradiation.[5] Recently, Kisch et al. doped TiO₂ with PtCl₄ during the sol−gel process to allow the degradation of 4-chlorophenol using visible light.[6] Several groups have also attempted to improve the efficiency of TiO₂ catalysts under band-gap irradiation (λ < 380 nm) via transition metal ion doping.[7−10] Wilke and Breuer doped TiO₂ with Cr^{3+} and Mo^{5+} during the sol−gel process and saw no improvement in photocatalytic activity over undoped TiO₂.[7] Martin et al. doped TiO₂ with V^{5+} via coprecipitation which resulted in catalysts with reduced photoreactivity.[8] Choi et al. found that doping with Fe^{3+}, Mo^{5+}, Ru^{3+}, Os^{3+}, Re^{5+}, V^{4+}, and Rh^{3+} increased photoreactivity in the liquid-phase photodegradation of CHCl₃, whereas doping with Co^{3+} and Al^{3+} decreased photoreactivity.[9] Recent reports indicate that vanadium doping provides a potentially promising strategy to improve the properties of photocatalytic materials. Anpo and co-workers recently described a V-doped TiO₂ photocatalyst prepared through ion implantation.[11] They found this physically doped

catalyst to be much more photoefficient than one prepared using traditional chemical techniques. Zhao and co-workers synthesized V-doped TiO₂ electrodes which generated a photocurrent under visible irradiation.[12]

We report on a simple photocatalyst preparation method to dope TiO₂ with V^{4+} sites, which has the effect of extending the wavelength range of the catalyst into the visible region. In this study, we focus on the gas-phase photocatalytic degradation of ethanol using two V-doped TiO₂ catalysts. The catalysts are composed of a monolayer coverage of TiO₂ combined with a submonolayer coverage of vanadium oxide (V^{4+}), both of which are supported on porous Vycor glass (PVG). The photocatalyst activity was assessed using ethanol, which is a sensitive surface probe.[13−15] The reactions were studied using ^{13}C solid-state NMR, which allowed an analysis of the products formed as a result of irradiation, as well as a determination of the relative catalyst activities.

Experimental Section

Catalyst Synthesis. All catalysts were supported on transparent porous Vycor 7930 borosilicate glass (PVG) obtained from Corning (BET surface area ∼250 m²/g). PVG supports (3.6 mm diam, 12 mm long, and 180 mg) were initially calcined under dry O₂ at 500 °C for 10 h, evacuated to 1×10^{-4} Torr, and then exposed briefly to the atmosphere upon transferring them to their respective catalyst preparation tubes. Four catalysts were prepared and studied: a TiO₂ monolayer catalyst supported on PVG (TiO₂/PVG), a 0.5 wt % vanadium oxide (V^{5+}) submonolayer catalyst supported on PVG (V/PVG), and two mixed oxide catalysts. The two doped catalysts were composed of a one-monolayer coverage of TiO₂ supported on a 0.5 V wt % V/PVG catalyst (TiO₂/V/PVG) and a 1.7 V wt % supported on one monolayer of TiO₂ (V/TiO₂/PVG).

The TiO₂/PVG catalyst was prepared on a vacuum rack via chemical vapor deposition (CVD) of TiCl₄, as we have previously described in detail.[16] The V/SiO₂ catalyst was prepared by immersing the PVG support overnight in a small test tube containing 90 μL of an ammonium metavanadate solution consisting of 1.0 g NH₄VO₃ dissolved in 50 mL of distilled water. Water was then removed by slowly heating the PVG in solution to dryness. The catalyst was further dried under vacuum at 140 °C for 2 h then calcined under dry O₂ for 10 h at 500 °C.

The TiO₂/V/PVG catalyst was prepared starting from a V/SiO₂ catalyst synthesized according to the above procedure.

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The V/SiO$_2$ catalyst was then transferred to a glass tube that could be closed to the atmosphere and evacuated. The tube included a sidearm to which TiCl$_4$ would be later added. Before the addition of TiCl$_4$, the preparation tube and support were initially heated under vacuum at 140 °C until the pressure inside the tube reached 5 × 10^{-5} Torr, which ensured a complete removal of water from the PVG. The tube containing the support was then transferred to a drybox for the addition of TiCl$_4$ in an amount that corresponded to a one-monolayer coverage (20 μL). TiCl$_4$ was then adsorbed onto the PVG by facile CVD.[17] After adsorption, the catalyst was exposed to the atmosphere and hydrolyzed overnight in distilled water. The catalyst was then dried at 140 °C for 3 h under vacuum and calcined under dry O$_2$ for 10 h at 500 °C.

The V/TiO$_2$/PVG catalyst was prepared by initially treating the PVG with TiCl$_4$ as described above. Upon TiCl$_4$ adsorption and subsequent hydrolysis, the catalyst was then immersed in 90 μL of NH$_4$VO$_3$ solution, dried, and calcined as described in the preparation of the V/PVG catalyst.

Sample Preparation and Characterization Methods. ^{13}C NMR samples were prepared and run in 5 mm sealed NMR tubes (Norell) at room temperature. Each catalyst was fitted with plastic endcaps for stability under magic angle spinning (MAS) conditions. The samples, including endcaps, were attached to a vacuum rack and dried under vacuum at 140 °C until the pressure inside the NMR tube reached 5 × 10^{-5} Torr. A total of 48 μmol of doubly ^{13}C-labeled CH$_3$CH$_2$OH (Cambridge Isotope Laboratories) and 96 μmol of O$_2$ were then introduced into the catalyst tube using a liquid N$_2$ bath. The sample was then sealed ~10 mm above the catalyst so it could be run under MAS conditions. ^{51}V NMR experiments were carried out on samples that were also dehydrated and run in sealed NMR tubes under static conditions at room temperature.

NMR analysis was performed on a 300 MHz Varian Unity-Plus spectrometer. A home-built MAS NMR probe (doubly tuned for ^{1}H and ^{13}C observation at frequencies of 300 and 75.4 MHz, respectively) was used for these experiments and has been described previously.[16] A 300W Xe arc lamp (ILC Technology) was chosen as the ultraviolet and visible light source. Two wavelength ranges were used in this study. The desired wavelength range was obtained through the use of a dichroic mirror (Oriel Corporation, 350−450 nm). A 396 nm cutoff filter was used in conjunction with the 350−450 nm mirror for the visible light only experiments. All samples were irradiated ex situ, followed by immediate NMR observations. The light power reaching the sample was estimated to be 3 W for the UV/visible studies and 2 W for the visible light only experiments. ^{51}V NMR experiments were performed with a 5 mm Chemagnetics static NMR probe.

ESR samples were prepared by drying the catalysts under vacuum at 140 °C in a 5 mm NMR tube equipped with a stopcock valve until the pressure in the tube reached 5 × 10^{-5} Torr. ESR spectra of dehydrated samples under vacuum were acquired using a Bruker ESP300E spectrometer operated at 9 GHz. UV−visible absorption spectra were recorded using a Cary 300 UV−vis spectrophotometer. The vanadium content of the mixture catalysts was determined by ICP analysis. XRD analysis was performed on a Siemens type-F diffractometer.

Results and Discussion

Catalyst Characterization. UV−visible absorption spectra (Figure 1) of vanadium containing TiO$_2$ photocatalysts exhibit a red-shift from undoped TiO$_2$ providing information on the mechanism of the mixed V−TiO$_2$ catalysts. Visible absorption
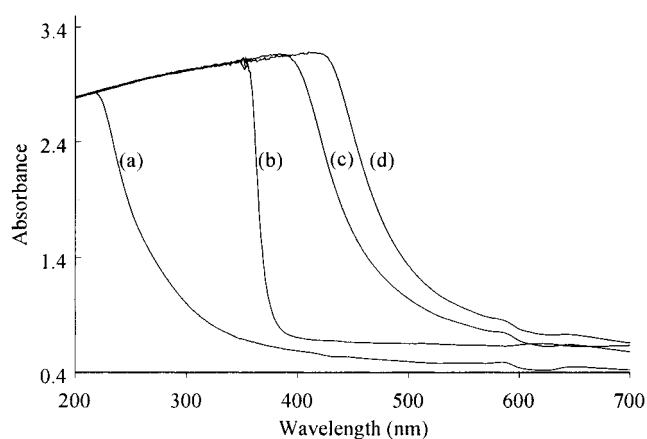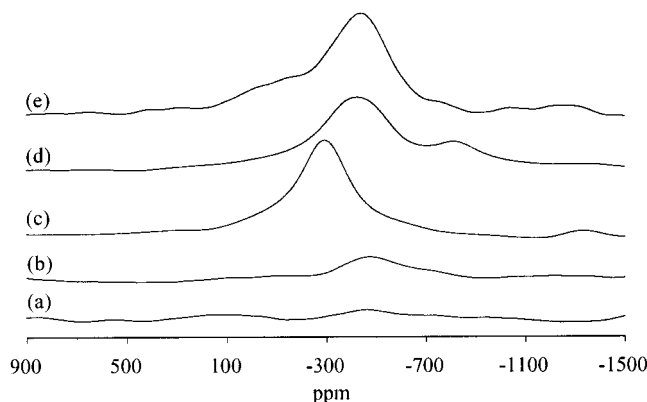

Figure 1. UV-visible absorption spectra of blank PVG and three TiO$_2$-based catalysts: (a) PVG, (b) TiO$_2$/PVG, (c) TiO$_2$/V/PVG, and (d) V/TiO$_2$/PVG.
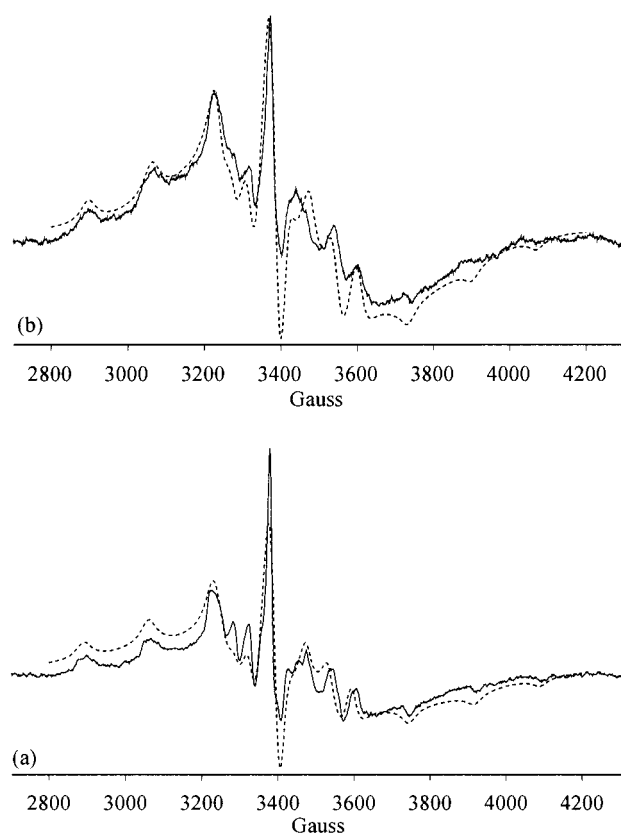
Figure 2. Experimental (—) and simulated (···) ESR spectra of (a) TiO$_2$/V/PVG and (b) V/TiO$_2$/PVG under vacuum at 100 K.

in these catalysts is indicative of the excitation of a 3d electron from a V^{4+} center into the TiO$_2$ conduction band.[18] It is believed that this photoexcited electron enables chemical reactions to occur at the surface of the V-doped catalysts in the presence of visible light because the oxidation of V^{4+} to V^{5+} occurs 2.1 eV below the TiO$_2$ conduction band.[18] The present mixture catalysts approach this value because they are able to absorb light in the range of 2.7−2.5 eV (Figure 1c,d).

ESR analysis of the mixture catalysts indicates the presence of at least two distinct V^{4+} species (Figure 2). The well-resolved signals from both catalysts indicates some vanadium may be present as an isolated species.[19] The hyperfine signal from the V/TiO$_2$/PVG catalyst could be satisfactorily simulated using the following parameters: $g_{\parallel} = 1.93$, $g_{\perp} = 1.96$, $A_{\parallel} = 166$ G, and $A_{\perp} = 51$ G. These values are similar to those reported by Gallay
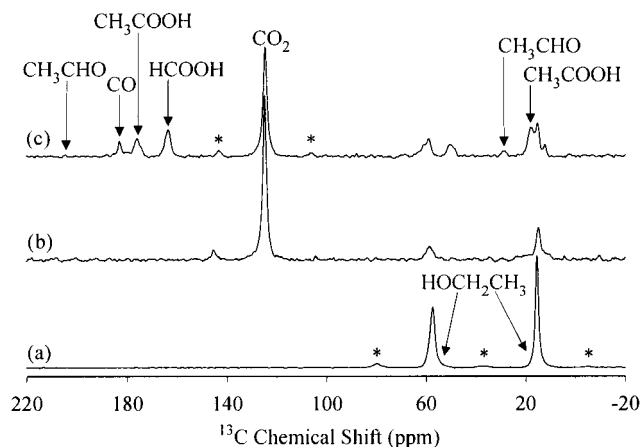
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Figure 3. Static ^{51}V NMR spectra of (a) TiO₂/V/PVG, (b) V/TiO₂/PVG, (c) V₂O₅ powder, (d) NH₄VO₃ powder, and (e) V/PVG. Chemical shift values were referenced to an external standard of liquid VOCl₃. A total of 200 000 scans were acquired using a Bloch decay pulse sequence with a 0.3 s recycle delay and a 1 μs pulse width.

Figure 4. Proton-decoupled ^{13}C Bloch decay MAS NMR spectra of ethanol before and after 1 h of irradiation with UV/visible light: (a) before irradiation, (b) after irradiation over TiO₂/PVG, and (c) after irradiation over V/PVG. Asterisks denote spinning sidebands of strongly adsorbed species. A total of 300 scans were acquired with a recycle delay of 3 s.

et al. for V⁴⁺ occupying interstitial sites in anatase TiO₂.[20] Similar ESR signals were observed by Martin and co-workers in V-containing TiO₂ colloidal particles calcined at 200 and 400 °C.[8] The signal from the TiO₂/V/PVG catalyst could be simulated with $g_{||}$ = 1.89, $g_{\perp}$ = 1.92, $A_{||}$ = 172 G, and $A_{\perp}$ = 48 G. Luca et al. reported similar values for substitutional V⁴⁺ centers in V-doped anatase TiO₂.[21] The broad underlying signal could be simulated using the first derivative of a Gaussian function. The resulting single line indicates the presence of a vanadium species comprised of aggregated V⁴⁺ sites with g values (g = 1.94 for TiO₂/V/PVG and g = 1.93 for V/TiO₂/PVG) close to those reported by Takahashi et al. for V₂O₅.[22] However, XRD data for these catalysts showed only a broad peak indicative of the amorphous nature of the Vycor support, presumably because of the low concentration of V on the PVG surface. As has been reported by Kol'tsov and co-workers[23] and as we have observed previously,[24] coverages of at least three supported monolayers of TiO₂ are necessary before resolved XRD spectra are obtained. At the low V loadings used in these experiments, it is not unexpected that the crystalline species are not detected in the XRD spectra, especially because the catalysts are comprised of only one or two monolayers.

The presence of V⁴⁺ in the mixture catalysts may be due to the reduction of V⁵⁺ by Ti³⁺ generated during the calcination of the catalysts. On the basis of his study of the solid-state preparation of V₂O₅/TiO₂, Trifiro proposed a mechanism for the spontaneous reduction of V⁵⁺.[25] Dehydroxylation of Ti⁴⁺ sites leads to the formation of Ti³⁺ followed by charge transfer to and subsequent reduction of V⁵⁺ to form stable Ti−O−V linkages. In their study of V₂O₅/TiO₂ catalysts, Herrmann and co-workers[26] proposed that, following calcination at 450 °C, V may become incorporated in tetravalent sites in the TiO₂ sublayers and form linkages similar to the findings of Trifiro. Both studies provide explanations for the reduction of V⁵⁺ we observe in the mixed catalysts because the Ti surface possesses a high concentration of hydroxyl groups and calcination was performed at a similar temperature (500 °C).

Solid state ^{51}V NMR spectra (Figure 3) of the mixed catalysts and two model compounds (V₂O₅ and NH₄VO₃ powder) were acquired in order to analyze the local structure of the vanadium species. V₂O₅ powder gives a single line at −293 ppm (Figure 3c). NH₄VO₃ exhibits two peaks at −423 and −811 ppm (Figure 3d). These chemical shift values are similar to those reported by Eckert and Wachs.[27] A comparison of the catalysts to the model compounds shows the V/PVG catalyst is composed of a

tetrahedral vanadium species (−440 ppm) similar to that of the precursor NH₄VO₃ along with a small amount of a V₂O₅ species (small shoulder at −200 ppm). Because the vanadium content of the mixed catalysts is primarily a V⁴⁺ species, which is paramagnetic and therefore not observable, these catalysts exhibit little to no ^{51}V NMR signal (Figure 3a,b).

TiO₂/PVG Catalyst. The ^{13}C NMR spectrum of ethanol before irradiation is shown in Figure 4a. The methyl (CH₃−) resonance appears at 15.5 ppm, whereas the peak at 58.0 ppm is assigned to the methylene (−CH₂−) carbon.[14] Peaks marked with an asterisk are spinning sidebands of strongly adsorbed ethanol species. After 1 h of UV/visible (350−450 nm) irradiation (Figure 4b), CO₂ (123.8 ppm) was the only product observed. In a previous study[14] on the same catalyst, carbon dioxide was observed along with the intermediate acetaldehyde under lower power UV/visible irradiation conditions. The TiO₂/PVG photocatalysis sample was then recalcined, reloaded with reagents, and irradiated with visible light. Oxidation of ethanol did not occur in this wavelength range in accordance with the fact that λ < 380 nm are required to activate TiO₂.

V/PVG Catalyst. It has been proposed that the catalyst preparation technique described above leads to a tetrahedral V⁵⁺ species (with one vanadium atom reacting with 3 OH groups at the surface of the PVG support).[28,29] Indeed no ESR signal was observed, which would otherwise indicate the presence of a V⁴⁺ species. Elemental analysis of the catalyst revealed a vanadium content of 0.5 wt %. Jonson proposed that isolated tetrahedral vanadium complexes form on SiO₂ surfaces at a coverage of 0.5 V wt %.[30] He also observed that the color of the catalyst changed from white to yellow when exposed to atmosphere, because of the coordination of water molecules,[31] then returned to white after moderate heating. The V/PVG catalyst in the present study behaves similarly.

The sample was first irradiated with visible light; however, no conversion of ethanol was observed. After calcination of this catalyst and sample reloading, a similar experiment was performed with UV/visible light. Previous studies have shown V/SiO₂ photocatalysts to be active under irradiation at 310−390 nm.[32−34] Charge separation involving the V=O bond is afforded by UV irradiation such that[32]

$$V^{5+} = O^{2-} \xrightarrow{h\nu} (V^{4+}\text{−}O^{-})*$$
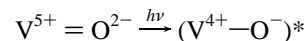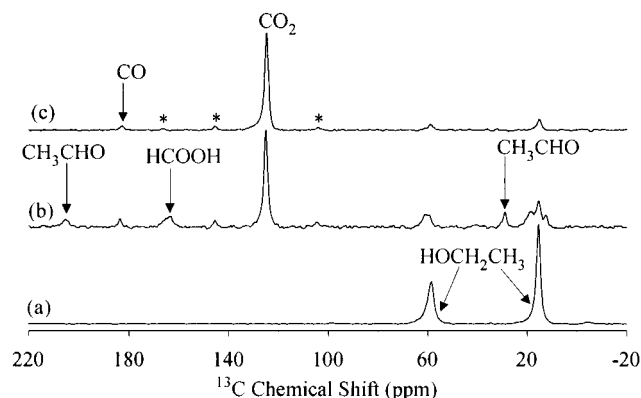
Figure 5. Bloch decay spectra of ethanol over TiO₂/V/PVG before (a) and after 1 h irradiation with visible (b) and UV/visible (c) light.

The subsequently generated electron−hole pair is responsible, through a charge transfer process, for the oxidation of organic probe molecules adsorbed on the catalyst surface. The presence of molecular oxygen is necessary for the reaction to proceed efficiently because O_2 acts to reduce the electron−hole recombination rate. O_2^- can initiate a variety of photooxidation reactions.

The spectrum acquired after UV/visible irradiation is shown in Figure 4c. After 1 h of irradiation, CH_3CHO (205.9 and 28.2 ppm), CO_2 (124.5 ppm), CO (182.7 ppm), HCOOH (163.1 ppm), and CH_3COOH (175.4 and 17.2 ppm) were observed. A similar product distribution was observed previously[35] in a study of ethanol over thermally catalyzed V_2O_5/SiO_2 where acetaldehyde, acetic acid, ethylene, carbon monoxide, and carbon dioxide were formed. Species appearing at 49.9 and 12.1 ppm have not been assigned.

Mixed TiO₂/V Catalysts. Under visible irradiation (Figure 5b), significant photoactivity was observed for the TiO₂/V/PVG catalyst in comparison with the V/PVG and TiO₂/PVG catalysts under identical conditions (396−450 nm). The observed products included: CH_3CHO (204.5 and 28.3 ppm), CO_2 (124.5 ppm), CO (183.0 ppm), and HCOOH (163.3 ppm) along with two unidentified peaks at 19.5 and 12.3 ppm. The V/TiO₂/PVG catalyst was slightly less active, because a small amount of CH_3COOH was also present after 1 h of visible irradiation.

Both mixture catalysts were more active under UV/visible irradiation, where only CO_2 and CO were observed (Figures 5c and 6c), than under visible irradiation. The mixed TiO₂/V/PVG catalyst presented activity and a product distribution comparable to TiO₂/PVG under UV/visible irradiation (Figures 4c and 5c). The V/TiO₂/PVG catalyst also showed considerable activity in oxidizing ethanol to CO_2 in the UV/visible wavelength range. However, it was somewhat less active than the other mixture catalyst (TiO₂/V/PVG), because carbon monoxide comprised about 40% of the product distribution after 1 h of irradiation (Figure 6c).

Under UV/visible irradiation, V^{4+} sites may act as charge recombination centers[8] in the mixed catalysts causing them to be only comparably (or less in the case of the V/TiO₂/PVG catalyst) photoactive in comparison with TiO₂/PVG under identical conditions. The V/TiO₂/PVG catalyst also exhibits a larger ^{51}V NMR signal than the TiO₂/V/PVG catalyst; therefore, fewer V^{5+} sites in V/TiO₂/PVG have been converted to V^{4+}. This may explain the decreased activity of this catalyst under visible light only irradiation where V^{4+} sites are considered active. The increased concentration of V^{5+} sites in the V/TiO₂/PVG catalyst also explains why this catalyst exhibits a product
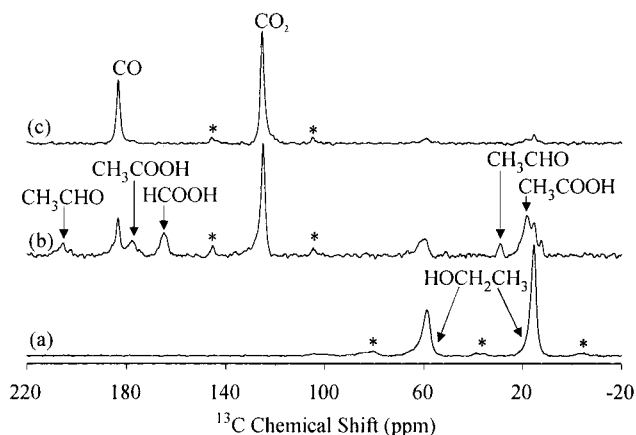
Figure 6. Bloch decay spectra of ethanol over V/TiO₂/PVG before (a) and after 1 h irradiation with visible (b) and UV/visible (c) light.

distribution similar to the V/PVG catalyst under UV irradiation conditions.

Conclusions

A V-doped TiO₂ photocatalyst that is active under visible irradiation has been synthesized using simple ambient chemical methods. It is believed that under visible irradiation excited vanadium centers donate an electron to the TiO₂ conduction band, which allows the oxidation of surface adsorbed molecules. The activity of the TiO₂/V/PVG photocatalyst is greatly increased in comparison with the monolayer TiO₂/PVG catalyst under visible only irradiation. Under UV/visible conditions, the photoactivity of the mixed catalyst is comparable to the TiO₂/PVG catalyst. Further improvement and studies of this catalyst may allow its utilization in conjunction with TiO₂ catalysts for better usage of available light sources. Future studies are also needed to fully understand these catalysts and to optimize the method of synthesis for use with other catalyst supports or surface morphologies.[15,36] The synthesis technique may also prove useful in altering the oxidation state of other dopant metal atoms.

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