of the C_{154}^+ ion with that of C_{60}^+ in Figure 2 and the abundance of the C_{154}^+ ion with those of the other ions in Figure 3. Although lower mass ions were ejected in order to allow enhanced mass resolution measurement of the Figure 3 spectrum, measurements under the same conditions, without ejection, showed that the $C_{154/60}$ ion ratio is similar to that in the Figure 2 spectrum. In view of these results, under conditions which are not expected to discriminate against detection of any ionic species (other than those specifically excluded), it seems likely that relative abundances are governed by kinetic effects in the soot formation process, rather than any "magic" stability of particular carbon aggregates.

Finally, in accord with previous observations that mass spectral abundances of carbon aggregate ions are critically dependent upon formation conditions,[14] C_{60}^+ appears with enhanced abundance when desorption from uncoated stainless steel is employed (Figure 1, but its relative abundance drops appreciably and those of aggregates containing more than 100 carbons are enhanced, when the soot is desorbed from the potassium chloride coated probe tip (Figures 2 and 3). This suggests factors other than the thermodynamic stability of C_{60}^+ are critical in determining its abundance (e.g., KCl assisted nucleation of carbon aggregates during soot formation in the low-temperature flame). Unfortunately, in common with all previous studies, the present observations neither refute nor confirm any particular structure hypothesis. However, comparison of our observations with those results, obtained under significantly different experimental constraints, could allow interpretation of the previous data with increased precision.

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Preparation of Highly Dispersed Anchored Vanadium Oxides by Photochemical Vapor Deposition Method and Their Photocatalytic Activity for Isomerization of *trans*-2-Butene

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Highly dispersed anchored vanadium oxide catalysts have been first prepared by using facile reaction of the photochemically activated $VOCl_3$ molecules with surface OH groups on Vycor glass. Anchored vanadium oxides prepared by photochemical method (photo-CVD) exhibit much higher yields in the phosphorescence with its long lifetimes (450 μs). These anchored vanadium oxides exhibit a higher activity for the photocatalytic isomerization reactions of 2-butene, as compared with those obtained for the oxides prepared by conventional impregnation method. A good linear relationship between the yields of photocatalytic isomerization and the yields of phosphorescence from the charge-transfer excited triplet state of the surface vanadyl species in tetrahedral coordination is obtained, indicating that not only the surface vanadyl species play a significant role in the photocatalytic reaction on vanadium oxide catalysts, but also a photochemical vapor deposition method leads to the higher dispersion of vanadium than impregnation method.

Introduction

For the complete understanding of photocatalysis, it seems inevitable to elucidate the chemical nature and reactivity of photoproduced electrons and holes, as well as the excited state of catalysts, including dynamics.[1] With well-defined chemically supported "anchored" catalysts, one can expect not only to achieve more active and selective catalytic and photocatalytic systems but also to obtain the detailed information on the true nature of active surface sites.

Chemical vapor deposition (CVD) method by using various reactive transition metal compounds has been extensively studied to prepare the anchored catalysts.[2] Photochemical activation of various transition-metal compounds adsorbed on support surfaces is also expected to be a promising method to prepare highly dispersed well-defined catalysts; however, there are rather few reports.[3]

In this paper we report that not only the advantage of the method of the photochemical activation of adsorbed $VOCl_3$ molecules to prepare the highly dispersed anchored vanadium oxides but also the significant role of the charge-transfer excited triplet state of vanadyl groups in the photocatalytic isomerization reaction of 2-butene on supported vanadium oxide catalysts.

Experimental Section

Preparation of Catalysts by Photochemical Vapor Deposition Method. Anchoring of $VOCl_3$ onto porous Vycor glass (Corning code, 7930; BET surface area, 155 m^2/g; major composition, SiO_2 $\doteq$ 96% and B_2O_3 $\doteq$ 3%) was performed using a facile reaction of photoactivated $VOCl_3$ with surface OH groups of the dehydrated Vycor glass specimen at 273 K. Photoactivation of adsorbed $VOCl_3$ molecules was carried out by UV excitation of the

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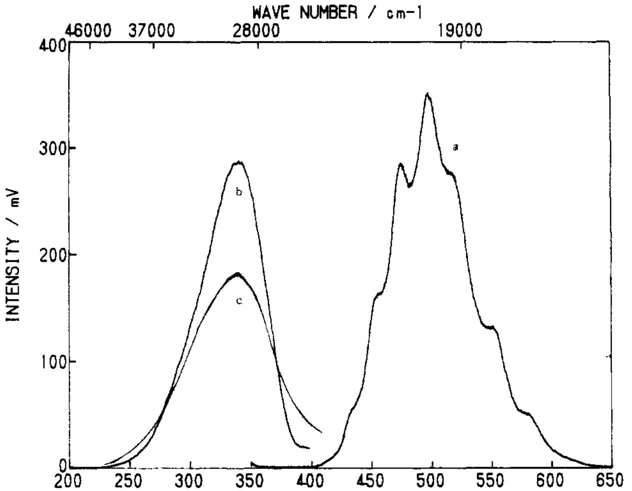


Figure 1. Phosphorescence (a) and its excitation spectrum (b) and UV absorption spectrum (c) of vanadium oxide catalyst anchored onto Vycor glass by photo-CVD method (phosphorescence was measured at 77 K; excitation was 280-nm beam for phosphorescence measurement; 500-nm emission was monitored for excitation spectrum measurement; UV absorption spectrum was measured at 298 K; content of vanadium was 0.1 V wt %).

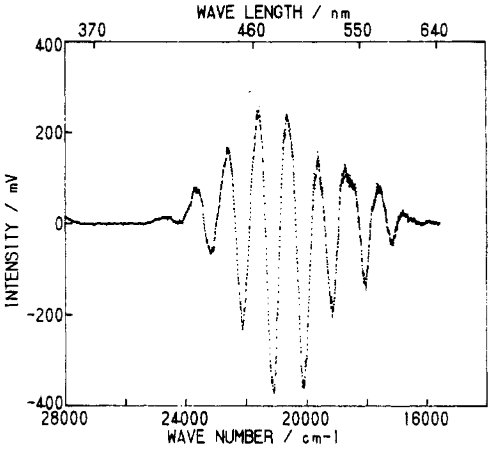
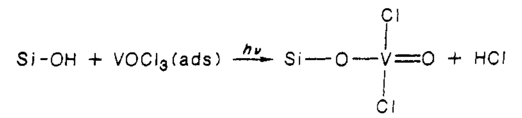


Figure 2. Second-derivative spectrum of the phosphorescence of vanadium oxide catalyst anchored onto Vycor glass by photo-CVD method (conditions were the same as those in Figure 1; accuracy was ±5 cm^{-1}).

charge-transfer absorption band of $VOCl_3$ molecules at approximately 300–450 nm (photo-CVD). The number of anchored $VOCl_3$ and reacted surface OH groups was monitored by UV (characteristic charge-transfer absorption band of vanadyl groups (V═O) at approximately 300–400 nm) and IR (O–H absorption bands at ~3750 cm^{-1}) spectroscopy, respectively. As HCl was generated during UV irradiation and V ═ O band remained, the following reaction would be involved in the anchoring reaction of $VOCl_3$.



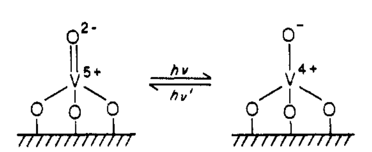
$$\text{Si-OH} + \text{VOCl}_3\text{(ads)} \xrightarrow{h\nu} \text{Si—O—}\overset{\text{Cl}}{\underset{\text{Cl}}{\text{V}}}\text{═O} + \text{HCl}$$

The advantage of this photo-CVD method is that it is easy to control the content of vanadium ions on the support by UV irradiation time and/or concentration of isolated surface OH groups on the support. Anchored samples were evacuated, hydrolyzed with H_2O, and then finally calcined in air.

Apparatus and Procedure. Dynamic photoluminescence studies were carried out at 77 and 298 K with a Shimadzu RF-501 spectrofluorophotometer equipped with a personal computer and an apparatus for lifetime measurements. The quartz cell with window and furnace sections, having a volume of about 50 cm^3, was connected to a conventional vacuum system (ultimate pressure of about 10^{-6} Torr (10^{-4} N/m^2)). The catalysts of 0.1–0.2 g was heated in air at 773 K, degassed at 723 K, heated at 773 K under 20 Torr of oxygen, and finally degassed at 423 K. The reactant butene was introduced onto the catalyst, its temperature being adjusted at 273 K. After then, UV irradiation of the catalyst in the presence of *trans*-2-butenes (6 Torr) was also carried out at 280 K, to minimize the dark reaction, using a high-pressure mercury lamp (Toshiba, SHL-100UV) through a color fileter and water filter 280 nm). At this temperature, the isomerization in the dark was very slow and negligible. The number of incident photons to the cell was determined by means of potassium ferrioxalate actinometry. The difference between the number of photons passing through the vanadium oxide/Vycor glass and the corresponding number with the pure Vycor glass gives the number of photons absorbed by the anchored vanadium oxide catalyst. Analysis of reaction products was made by gas chromatography.

Results and Discussion

Phosphorescence of Vanadium Oxide Anchored onto Vycor Glass. Figure 1a shows the typical phosphorescence spectrum at 77 K of anchored vanadium oxide prepared by photo-CVD method with its corresponding excitation spectrum. These phosphorescence and excitation (absorption) spectra are in good agreement with those obtained with supported V/SiO_2 oxides prepared by conventional impregnation method[4] and are attributed to the following charge-transfer processes on surface vanadyl groups (V═O) of tetrahedral VO_4 unit structure, involving an electron transfer from O^{2-} to V^{5+} and a reverse radiative decay.[4,5,6]



(1)

Figure 2 shows the second-derivative spectrum of the phosphorescence shown in Figure 1a. The spectrum indicates that the energy gap between the (0 → 0) and (0 → 1) transition bands is to be 1027 cm^{-1}, being in good agreement with the vibrational energy of surface V═O bond obtained by IR measurement. This shows the photon energy absorbed is mainly localized on the V═O surface bonds.[4,5]

Phosphorescence of anchored vanadium oxide prepared by the photo-CVD method, which increased linearly in intensity with the content of anchored vanadium ions, decayed as a beautiful single exponential. The lifetime was determined to be 8.2 ms at 77 K and 450 μs at 298 K, respectively. These values scarcely changed with increasing the content of anchored vanadium ions, at least up to 1 V wt %. These values were found to be much longer than those of impregnated vanadium oxides, in which the lifetimes become shorter with the content of vanadium ions.[7,8] These results suggest that vanadium ions are highly dispersed on anchored vanadium oxide prepared by the photo-CVD method, even at higher vanadium contents. Being in agreement with this conclusion, a preliminary phosphorescence quantum yield at 77 K was found to be approximately 0.35, while that of the impregnated vanadium oxide was less than 0.1.[9]

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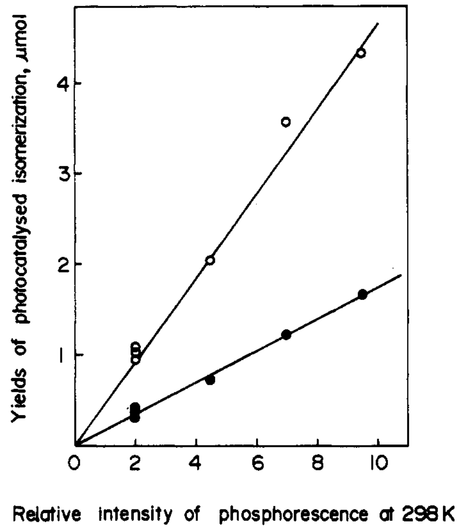

Figure 3. Relationship between the yields of phosphorescence of vanadium oxide catalysts anchored onto Vycor glass and the yields of photocatalyzed isomerization of *trans*-2-butene on these catalysts (yields of phosphorescence were measured at 280 K; temperature of the photocatalyzed reactions on the catalysts was 298 K; ○, yields of *cis*-2-butene; ●, yields of 1-butene; initial pressure of *trans*-2-butenes was about 3.0 Torr).

Photocatalyzed Isomerization of Butenes on Anchored Vanadium Oxide. The photocatalyzed isomerization reaction has been extensively studied with a view to understanding the true nature of the active surface sites on metal oxide catalysts.[7,11,12] UV irradiation of anchored vanadium oxide in the presence of *trans*-2-butenes was found to lead to trans → cis (geometrical) and 2 → 1 (double bond shift) isomerization reactions even at a lower temperature than 273 K. The yields of these reactions increased with the UV irradiation time. As shown in Figure 3, the rate of photocatalyzed isomerization is in a good linear relationship with the yields of phosphorescence, directly indicating that the charge-transfer excited triplet state of surface vanadyl groups play a significant role in the photocatalyzed isomerization reaction. In fact, the lifetime of the phosphorescence was found to decrease in the presence of 2-butenes, its extent depending on the pressure of butenes. It is likely that the interaction of the excited triplet state of $(V^{4+}-O^{-})^{*}$ paired state or the O^{-} species of the paired state with *trans*-2-butene results in opening of its C=C bond and resulting intermediate species participate in the geometrical isomerization of 2-butene, in a manner similar to that proposed for the photocatalyzed isomerization of 2-butenes over TiO_2,[11,12] MgO,[13] and supported V_2O_5/SiO_2.[5,7]

These results showed remarkable contrast with those obtained with impregnated vanadium oxide catalysts, in which the yield of the photocatalyzed isomerization as well as the yield of the phosphorescence increased first with the content of vanadium ions and then decreased, even in the region of less than 0.1 V wt %, for higher vanadium contents by an increase of radiationless deactivation due to the growth of aggregation of vanadium oxide species.[1,5,7] Thus, the present work not only provides useful information on the advantage of the photo-CVD method to prepare the highly dispersed anchored catalysts and to achieve high photocatalytic activity but also directly shows the significant role of the charge-transfer excited triplet state in the photocatalytic reaction on supported vanadium oxides.

Conclusion

Highly dispersed anchored vanadium oxide catalysts were first prepared by photochemical vapor deposition method using $VOCl_3$. Photochemically activated $VOCl_3$ molecule easily reacted with surface OH groups on Vycor glass. Photochemically anchored vanadium species were transferred to tetrahedrally coordinated anchored vanadium oxide species by calcination in oxygen atmosphere. Anchored vanadium oxides prepared by photochemical method (photo-CVD) exhibit much higher yields in the phosphorescence due to its longer lifetimes. These anchored vanadium oxide catalysts also exhibited a much higher activity for the photocatalytic isomerization reactions of 2-butene with quantum yield of about 0.28, as compared with those obtained for the oxides prepared by conventional impregnation method where quantum yield was less than 0.1. A good linear relationship between the yields of photocatalytic isomerization and the yields of phosphorescence from the charge-transfer excited triplet state of the surface vanadyl species in tetrahedral coordination was obtained. These results appears not only to provide useful information on the advantage of the anchored oxide catalysts prepared by photo-CVD method, i.e., a surface photochemical reaction achieves the higher dispersion of vanadium by preventing the vanadium entities from gathering during subsequent calcination, but also directly showed the significant role of the charge-transfer excited triplet state in the photocatalytic reaction on supported vanadium oxides.

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