sites in the modified DNA may also contribute to these differences. All of these results clearly show that AM modification of the DNA minor groove greatly limits daunorubicin binding.

Wild type T4 DNA has glucose residues covalently attached to cytosine in the major groove.[16] The glucose adduct is uncharged, does not significantly perturb the double-helix structure, and should be a steric probe for the major groove. We have isolated both this DNA[17] and a nonglucosylated sample.[18] In contrast to the results with AM-modified DNA samples, binding of daunorubicin to the glucosylated DNA is quite similar to binding to the nonglucosylated T4 mutant DNA (Figure 1B). Viscometric titrations with the glucosylated DNA are not significantly different than with the nonglucosylated DNA samples (not shown), and it is clear that the glucose residue in the major groove has a negligible effect on daunorubicin binding to DNA. These results taken together demonstrate that daunorubicin strongly prefers an intercalation complex in which the A-ring substituents are located in the DNA minor groove.

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Registry No. Daunorubicin, 20830-81-3.

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Diffuse Reflectance Infrared and Photoluminescence Spectra of Surface Vanadyl Groups. Direct Evidence for Change of Bond Strength and Electronic Structure of Metal-Oxygen Bond upon Supporting Oxide

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In the present communication, evidence is presented demonstrating that the bond strength and electronic structure of metal-oxygen bonds in supported metal oxides are dependent on the kinds of carriers and contents, with V=O double bonds in vanadium oxide as an example. Although much effort has so far been made to clarify surface structures and properties of catalytically active components supported on various carriers, results, as reported in the present study, have never reported. The present work will be useful for an understanding of catalytic reactions including photocatalysis and for solid inorganic chemistry.

The absorption bands of V=O double bonds in various supported vanadium oxides, which were changed along with the carriers and contents, are summarized in Table I.[1] The bond lengths listed in Table I were calculated on the basis of the correlation between the wavenumbers of V=O bonds and their bond lengths.[2] Byström et al.[3] and Bachmann et al.[4] have reported 1.58 Å for the V=O bond length in V_2O_5 crystals by their X-ray analyses, which is slightly longer than the present value determined by the diffuse reflectance IR technique. As shown in Table I, there are two kinds of V=O species in supported vanadium oxides. One has a length of 1.55-1.58 Å, the other of 1.68-1.70 Å. By considering that lengths of V-O single bonds in V_2O_5 crystals are 1.78-2.02 Å,[3,4] it follows that the latter V=O species is weaker in bond strength than that in the V_2O_5 lattice but it still retains the property of a double bond.

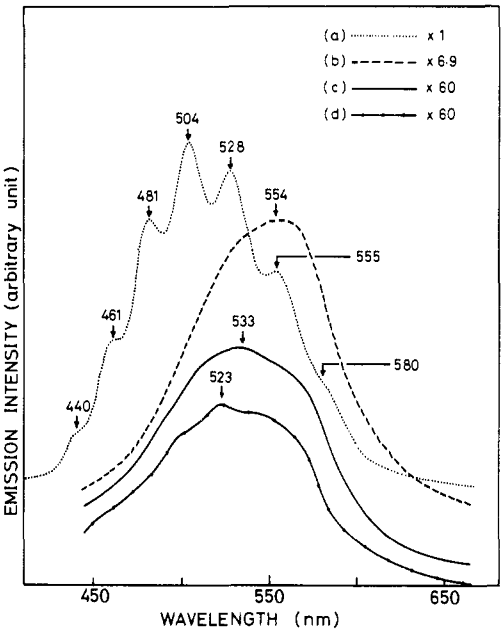

Figure 1. Phosphorescence spectra of 3.3 wt % V_2O_5/SiO_2 (a), 5.1 wt % V_2O_5/MgO (b), 5.3 wt % $V_2O_5/\gamma\text{-}Al_2O_3$ (c), and 5.1 wt % $V_2O_5/\alpha\text{-}Al_2O_3$ (d) at 77 K. The spectra were recorded at 77 K after evacuation of the samples at 673 K. Excitation wavelengths were listed in Table I. Slit widths for excitation and emission were 5.0 and 1.5 nm, respectively.

Generally, the strengths of metal-oxygen bonds decrease with decreasing electronegativity of metal ions.[5] The addition of electron-donating metals such as alkaline metals into pure V_2O_5 has indeed been reported to cause a red shift of the stretching band of V=O groups.[6] A similar red shift has been observed in the solid solutions of V_2O_5-MoO_3 because the charge of vanadium ions has been changed in part of 4+ from the usual 5+ owing to the presence of 6+ molybdenum ions in the V_2O_5 lattice.[7] Therefore, the bands at 912-954 cm^{-1} presumably result from V=O species in which the charges of vanadium ions are less than 5+. Magnesia is known to be a typical basic oxide,[8] and the V=O stretching band appeared at 922 cm^{-1} on the oxide. It is probable that silica gel has both basic and acidic sites on the surface. The V^{4+} ions were confirmed in a separate ESR experiment to exist in the V_2O_5/TiO_2 sample without any reduction treatment,[9] which is the reason for the appearance of the V=O band at 912 cm^{-1}.

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(1) Supported vanadium oxides were prepared by the following impregnation method. Silica gel (Fuji Davison Chemical, ID type) or other supports were soaked in an ammonia-aqueous solution of ammonium metavanadate, and water was evaporated on a water bath. The sample obtained was then calcined in air at 873 K for 5 h. The V_2O_5 content was determined by an atomic absorption spectroscopy after the sample was dissolved in a concentrated HCl + HNO_3 solution. Diffuse reflectance IR and photoluminescence spectra were measured by using a Nicolet 7199C FTIR spectrometer at 300 K and a Hitachi 650-10s fluorescence spectrophotometer at 77 K, respectively.

(2) On the basis of bond lengths and wavenumbers of vanadyl groups in $VOCl_3$, V_2O_5, $VOSO_4 \cdot 5H_2O$, $(NH_4)_2[VO(NCS)_4 \cdot H_2O] \cdot 4H_2O$, and $V_2O_4 \cdot 2H_2O$, one can obtain the following linear correlation, bond length (Å) = 2.751 - 0.001 15 × wavenumber (cm^{-1}).

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Table I. Diffuse Reflectance Infrared and Photoluminescence Spectra of Surface Vanadyl Groups

support	content, wt %	wavenumber[a] of V=O, cm^{-1}		bond length[b] of V=O, Å		photoluminescence[a] E_X^{max}, nm	E_M^{max}, nm	intensity[c]
none	100	1026		1.571				0
SiO_2	1.0	1035	927	1.561	1.685	320	501	0.56
	3.3	1035	927	1.561	1.685	320	504	1.00
	4.2	1035	927	1.561	1.685	320	504	0.50
	7.2	1035	937	1.561	1.673	323	506	0.87
	8.0	1035	943	1.561	1.667	323	511	0.19
	13.6	1032	943	1.564	1.667	323	522	0.19
	29.8	1032	954	1.564	1.654	323	524	0.16
γ-Al_2O_3	5.3	1016		1.583		323	533	0.02
α-Al_2O_3	5.1	1043		1.552		295	523	0.02
MgO	5.1		922		1.691	320	554	0.12
TiO_2	5.2		912		1.702			0

[a] See footnote 1 in the text. [b] See footnote 2 in the text. [c] Relative intensity at 77 K.

The shapes and intensities of the phosphorescence spectra of the supported V_2O_5 samples were strongly dependent on the kinds of supports and the contents, as shown in Figure 1 and Table I.[1,10] The V_2O_5 and V_2O_5/TiO_2 samples did not show any phosphorescence spectra. This phosphorescence is attributed to the electron-transfer process from $T_1(V^{4+}–O^-)$ to $S_0(V^{5+}=O^{2-})$, resulting in the disappearance of pairs of hole centers (O^-) and trapped electrons (V^{4+}).[11,12] Although the presence of fluorescence has been previously reported on V_2O_5, MoO_3, and WO_3 supported on porous Vycor glass,[12,13] no fluorescence has been observed in the present study, in conformity with the results on V_2O_5/SiO_2 and MoO_3/SiO_2 by Kazansky et al.[11] and Iwasawa et al.[14]

As shown in Figure 1, the phosphorescence spectrum from V_2O_5/SiO_2 has a well-resolved vibrational structure. The energy separation of the vibrational bands in the spectrum is in agreement with the surface vanadyl groups. For example, the separation between the 0–0 (440 nm) and 0–1 (461 nm) transitions corresponds to an energy of 1035 cm^{-1}, which was the same as that observed in the IR measurement. It is concluded from the spectra, using the Franck–Condon principle,[15] that the nuclear distance of the $V^{5+}=O^{2-}$ complex will become longer in the excited states. The intensity of phosphorescence from V_2O_5/SiO_2 showed a volcano-shaped dependence on the degassing temperatures of the sample.[10] The intensity increased steadily from 300 to 573 K. This is ascribed to a decrease of quenching by adsorbed oxygen.[12,16] On the other hand, the phosphorescence decreased to a certain extent with heightening the evacuation temperatures from 573 to 773 K. Such behavior is due to desorption of oxygen from the V=O bonds.[12]

The present results are helpful in understanding heterogeneous catalysis. For example, one-step hydroxylation of benzene to phenol using N_2O as an oxidant has very recently been reported over V_2O_5-containing catalysts.[17] The promoting effect of carriers on the phenol formation was $SiO_2 \gg MgO > \gamma\text{-}Al_2O_3 > \alpha\text{-}Al_2O_3 \simeq TiO_2$. It was also found that 1–10 wt % V_2O_5 content on SiO_2 was effective, the maximum yield of phenol being achieved at 3.3 wt %.[17] It is of significant interest to note that the catalytic activities are roughly proportional to the relative intensities of phosphorescence. This suggests that the vanadyl groups evolving phosphorescence act as active sites for the phenol synthesis or that O^- species in the $T_1(V^{4+}–O^-)$ state, which may be formed through the reaction $V^{3+} + N_2O \rightarrow V^{4+}–O^- + N_2$ during the catalytic run, is an active oxygen-yielding phenol from benzene. In photocatalysis, Yoshida et al.[18] have found that photocatalytic oxidation of CO proceeds over V_2O_5/SiO_2 but scarcely over V_2O_5/Al_2O_3. Taking into consideration that the $T_1(^{4+}–O^-)$ species is active for this reaction,[12] the results by Yoshida et al. are clarified by the present findings. Similar discussion is possible for the photocatalytic oxidation of propene.[19]

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Registry No. SiO_2, 7631-86-9; Al_2O_3, 1344-28-1; TiO_2, 13463-67-7; MgO, 1309-48-4.

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(10) After being mounted in a quartz cell, the V_2O_5-containing sample was evacuated at 773 K for 2 h, exposed to oxygen (P_{O_2} = 13.3 kPa), and cooled down to ambient temperature in the presence of oxygen. Subsequent to this pretreatment, the sample was degassed at increasing, stepwise, temperatures and subjected to the photoluminescence measurement at 77 K.

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Vinyl Radical Cyclization. 2. Dicyclization via Selective Formation of Unsaturated Vinyl Radicals by Intramolecular Addition to Triple Bonds. Applications to the Synthesis of Butenolides and Furans

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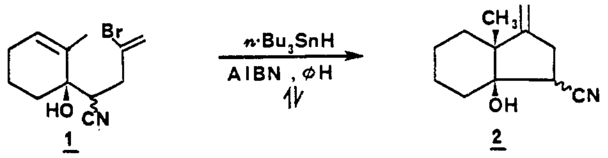
We have recently shown[1] that the cyclization of vinyl radicals is a valuable synthetic method illustrated, inter alia, by the transformation of 1 to 2.



1 2

The compatibility with unprotected functional groups such as the free hydroxyl of 1 and the relative insensitivity to steric hindrance that allows the formation of bonds resulting in quaternary centers will undoubtedly be found to be general features of most radical cyclization processes. Additionally, the vinyl radical cyclization has the chemically valuable feature that the resulting ring has a double bond in a predetermined position.

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