$$M + e^- \rightarrow M^+ + 2e^- \qquad (2)$$

as a matrix. In particular, Franck-Condon restrictions are expected to be more relaxed in the former case so that electron transfer could take place with a slight change of geometry. Thus, cations generated by reaction 1 are likely to be formed in a less reactive condition (i.e., with less vibrational energy) than those produced in reaction 2.

It is suggested that the above considerations can plausibly account for our results showing the formation of the HME radical cation in the FM matrix but not in the HME matrix, even when electron scavengers are incorporated in the latter. Some support for this interpretation comes from the detection of the neutral radicals $\cdot CMe_3$ and $\cdot CMe_2CMe_3$ after irradiation of the HME matrix containing SF_6 (Figure 2), since these two radicals may well be produced by the dissociation of vibrationally excited HME cations. Also, the radical $\cdot CH_2CMe_2CMe_3$ which is also present could be formed by proton transfer from the parent cation to a neighboring HME molecule.

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ARTICLES

Modified Electronic Structure and Enhanced Catalytic Activity of Cobalt Tetraphenylporphyrin Supported by Titanium Dioxide

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The electronic structure and the catalytic activity of cobalt tetraphenylporphyrin supported on titanium dioxide ($CoTPP/TiO_2$) were studied in order to reveal the electronic interaction between the oxide and the planar complex, which can modify the nature of the latter substance. $CoTPP/TiO_2$ showed a sharp isotropic ESR signal at a g value of 2.003 and a UV band around 590 nm, values which were completely different from those of the unsupported CoTPP. The formation of an anionic radical, which has an odd electron in the porphyrin ring, is suggested. $CoTPP/TiO_2$ showed remarkable catalytic activity for the reduction of nitric oxide to nitrous oxide and molecular nitrogen even at 50 °C with hydrogen, which was found to be adsorbed on $CoTPP/TiO_2$. The activity was much accelerated at 150 °C, where a successive reduction of nitric oxide in the sequence $NO \rightarrow N_2O \rightarrow N_2$ was clearly indicated.

Introduction

It has been recognized for a long time that certain supports play essential roles in heterogeneous catalytic and photoelectric reactions. Metal porphyrin molecules, square planar complexes which are extensively studied as oxygen carriers,[1] can offer one of their axial sites to be adsorbed on some catalyst supports such as alumina. Although the adsorption states of organic molecules on oxides have been extensively studied by means of various spectroscopy,[2] there have been few reports on the electronic perturbation of metal porphyrin molecules supported on oxides, a process which is expected to modify their electronic and catalytic properties. Very recently, Fan and Bard[3] described the spectral sensitization and the catalytic activity of phthalocyanine-coated titanium dioxide.

In the present study, we report on the modified electronic structure and the enhanced catalytic activity of cobalt tetraphenylporphyrin supported on titanium dioxide ($CoTPP/TiO_2$) for the reduction of nitric oxide, which was reported to be catalyzed by CoTPP.[4] This oxide is expected to modify the nature of the adsorbed molecule by transferring its electron to the CoTPP molecule as a n-type semiconductor.[5] Recently, some interesting behavior of the oxide as the catalyst support was reported,[6] although the interaction mechanism has not been revealed.

Experimental Section

CoTPP was prepared according to the literature.[7] Titanium dioxide (TiO_2) was obtained from Titan Industry, Ube, Japan. It was believed to be prepared from titanium sulfate. When TiO_2 was immersed in red-purple solution of CoTPP in benzene, a green slurry of CoTPP/TiO_2 was formed; 5 wt % of CoTPP was supported on TiO_2. Metal-free porphyrin (H_2TPP) on TiO_2 was prepared similarly.

After the materials were dried under vacuum at room temperature, the electronic and ESR spectra were observed by the diffuse reflectance and powder methods, respectively, using Shimazu UV-202 and JEOL JES-FE1X.

The catalytic activity for the reduction of nitric oxide with hydrogen was measured at 50 and 150 °C by using a conventional circulating reactor (800 mL) with a fixed catalyst bed in which a thermowell was located. The circulation rate was ca. 500 mL/min at atomospheric pressure, which was attained by a magnetically driven piston. Partial pressures of NO, H_2, and Ar (internal standard) were 2, 60, and 1 cmHg, respectively. The catalyst weight and the bed height were 4 g and 1 cm, respectively. Yields of N_2, N_2O, and NH_3 were determined by periodical sampling (5 mL) and analysis with a gas chromatograph, using columns packed with molecular sieve 13X, Porapack-Q, and 1-hendecanol/liquid paraffin on Flusin T, respectively. The amount of adsorbed NO was estimated from the difference of the mass balance as for nitrogen in the closed reactor.

Results and Discussion

Spectroscopic Profiled of CoTPP/TiO_2. The ESR signals of CoTPP/TiO_2 under vacuum at 77 K are shown in Figure 1, where the signal of CoTPP in an acetone–benzene mixture is also illustrated. CoTPP in acetone–benzene gave a signal (g = 1.996) with hyperfine structure due to the interaction of an odd electron in the d_{z^2} orbital of cobalt with its nuclear spin ($I = {}^7/_2$) (Figure 1A). This profile may be attributed to the oxygen adduct as observed with cobalt tetra(p-methylphenyl)porphyrin.[8] Solid CoTPP dispersed in H_2TPP was reported to show essentially the same signal as that of its oxygen-free state in the solution.[9]

In contrast, a completely different signal (g = 2.003, 6.4 G for peak-to-peak width) without hyperfine structure was observed for the green slurry of CoTPP/TiO_2 (Figure 1B). A sharp signal may indicate the great extent of dispersion of CoTPP on TiO_2. TiO_2 itself showed a signal (g = 1.914) ascribed to trivalent titanium ion; however, it was weak and was indifferent to the signal shown in Figure 1. A similar signal appeared for H_2TPP/TiO_2. Its g value and line width were 2.003 and 5.9 G, respectively (Figure 1C).

These isotropic signals are assigned as coming from the free electron which can be assumed to be located in the porphyrin π orbital.[1] An anion radical prepared from H_2TPP ($H_2TPP^{-}\cdot$) by electrochemical reduction was reported to show a signal with a line width of 3.8 G and a g value of 2.0027.[10] A cation radical prepared electrochemically from H_2TPP ($H_2TPP^{+}\cdot$) was reported to display an anisotropic signal ($g_\parallel$ = 2.0085 and $g_\perp$ = 2.0127) at 77 K, although it gave an isotropic one (g = 2.0111) at room temperature.[11] $CoTPP^{-}\cdot$, prepared by electrolysis, was reported to give an isotropic signal (g = 2.003, line width = 5.7 G).[12] Co^{III}TPP, the first oxidation product of Co^{II}TPP, reportedly lost the ESR signal.[11] Thus, we conclude that the isotropic signals observed with H_2TPP/TiO_2 and CoTPP/TiO_2 come from their anion radicals.

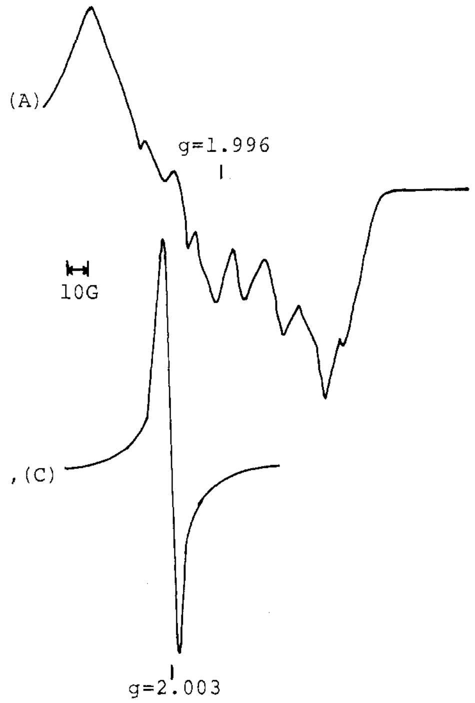

Figure 1. ESR spectra of (A) CoTPP in benzene–acetone solution, (B) CoTPP/TiO_2 powder, and (C) and H_2TPP/TiO_2 powder. Spectra were observed at 77 K after 1-h evacuation at room temperature except for (A).

One-electron transfer from TiO_2 to the porphyrin ring may induce a triplet state in CoTPP/TiO_2. In such a case, either an anisotropic or no signal is expected.[11] However, a completely isotropic signal was observed for CoTPP/TiO_2 at 77 K. Felton et al.[10b] reported that the central metal ion was chemically or electrochemically reduced at the first step. Furthermore, $CoTPP^{-}\cdot$ showed a signal very similar to that of CoTPP/TiO_2 as mentioned above.[12] These facts may suggest that the partial reduction of cobalt ion as described by $Co^{2-\delta}$ as well as one-electron transfer to the porphyrin ring take place in the CoTPP/TiO_2 system.

Diffuse reflectance electronic spectra of H_2TPP/TiO_2 and CoTPP/TiO_2 are shown in Figure 2, where those of CoTPP in benzene and on silica gel are also included. Supporting CoTPP on silica gel induced slight shifts of visible (536 nm) and Soret (420 nm) bands, which can be explained in terms of polarization due to physical adsorption. Considerable red shifts of both bands were observable as for CoTPP/TiO_2, indicating a strong interaction between TiO_2 and the porphyrin ring. A band around 590 nm is considered characteristic for the ionic radical of the porphyrin complex. H_2TPP/TiO_2 (Figure 2) showed a sharp adsorption band at 653 nm and a Soret band at 435 nm, respectively. The relative intensities of four bands in the visible region were completely the reverse of those of H_2TPP in benzene, although their positions were the same. Such spectra may suggest, being compared with those of H_2TPP and CoTPP reduced electrochemically,[12,13] that anion radicals are derived from the compounds supported on TiO_2.

CoTPP extracted from CoTPP/TiO_2 with benzene gave the same profile of electronic spectrum as that of original CoTPP in benzene, suggesting the reversible nature of electronic modification brought about by support on TiO_2.

Catalytic Activity of CoTPP/TiO_2 for the Reduction of Nitric Oxide. Reaction profiles of NO reduction (eq 1)

$$4NO + 3H_2 \rightarrow N_2O + N_2 + 3H_2O \qquad (1)$$

catalyzed by CoTPP/TiO_2 are shown in Figures 3 and 4,

TABLE I: Catalytic Activity of $CoTPP/TiO_2$ for Nitric Oxide Reduction[d]

type of reaction	catalyst	reaction temp, °C	consumed NO,[a] %	product yield,[b] % N_2O	product yield,[b] % N_2	adsorption of NO[c]
with hydrogen of 60 cmHg	$CoTPP/TiO_2$	50	57	5	0	52
	$CoTPP/TiO_2$	150	100	100	0	0
	TiO_2	150	9	11	1	7
without hydrogen	$CoTPP/TiO_2$	50	55	2	0	53
	$CoTPP/TiO_2$	150	82	55	15	12

[a] Determined by a gas chromatograph after the reaction of 5 h. [b] No production of ammonia was ascertained. [c] Nitric oxide base. [d] Reactions were performed in a closed circulating reactor. Catalyst (CoTPP on TiO_2: 5 wt %) used: 4 g, P_{NO} = 2 cmHg.

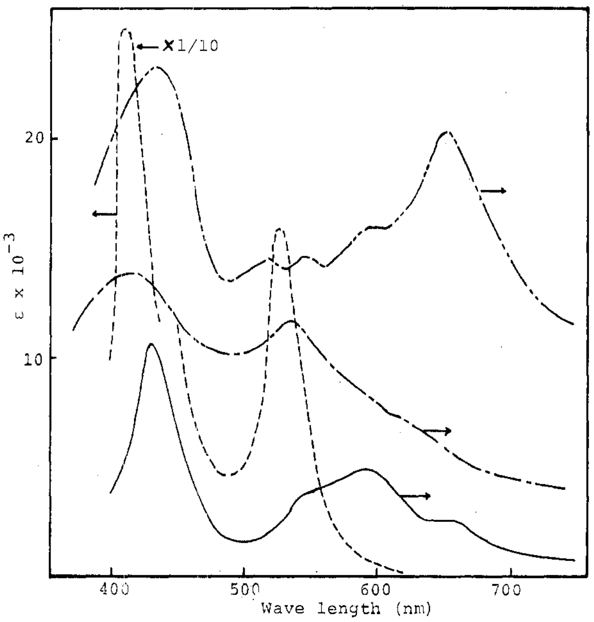

Figure 2. Electronic spectra of (- - -) CoTPP in benzene, (— - —) $CoTPP/SiO_2$ powder, (—) $CoTPP/TiO_2$ powder, and (— - - —) H_2TPP/TiO_2 powder.

where the reaction temperatures were 50 and 150 °C, respectively. At 50 °C, the major reaction was the adsorption of nitric oxide (calculated from the nitrogen balance after no ammonia in the gas phase was ascertained), which was very rapid, being saturated by 10 min. Although the formation of nitrous oxide or molecular nitrogen was minor, it should be noted that the reduction occurred at as low as 50 °C. Because of the small extent of reduction, the amount of adsorption was almost constant at the level of 50% of introduced nitric oxide during the reaction. The level corresponds to a NO/complex mole ratio of 2, indicating the formation of a dinitrosyl adduct on $CoTPP/TiO_2$. The dinitrosyl adduct was reported to be formed on ruthenium complex.[14] The catalyst used in the reaction at 50 °C showed the same activity for the formation of nitrous oxide and molecular nitrogen in the second run after the evacuation at the same temperature as observed in the first run; however, the level of adsorption (ca. 23%) of introduced nitric oxide was considerably decreased in the second run. The latter fact may suggest that the adsorption of nitric oxide on $CoTPP/TiO_2$ is quite stable at this temperature so as not to be removed.

Raising the reaction temperature increased the rate of N_2O formation markedly and decreased the level of NO adsorption. The rate of N_2O formation at 150 °C was 4.3×10^{-2} mmol (g of catalyst)$^{-1}$ h^{-1}. No reaction was observable on unsupported CoTPP at this temperature under the same conditions.[15] The NO adsorption reached the level of 25% (of introduced NO) at the initial stage of reaction within 2 min, the rate of adsorption being also markedly accelerated at this temperature by support on TiO_2. The level of adsorption remained constant for 2 h and then started to decrease when the conversion reached 40%, indicating that the adsorption is ruled out as the rate-determining step. The level of adsorption at this temperature corresponds to the NO/Co mole ratio of unity, being half of the value at 50 °C. The ratio suggests a single molecule of nitric oxide coordinated on CoTPP at this temperature.

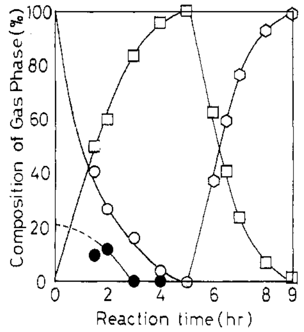

Figure 3. Reduction profile of nitric oxide over $CoTPP/TiO_2$ at 50 °C: partial pressures of NO and H_2, 2 and 60 cmHg; catalyst, 4 g; (○) NO; (□) N_2O; (●) adsorbed NO. All compositions were based on introduced NO.

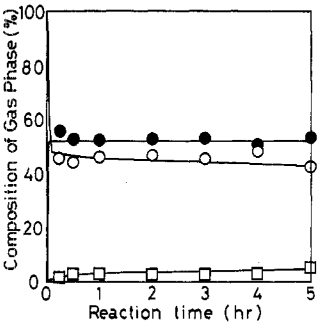

Figure 4. Reduction profile of nitric oxide over $CoTPP/TiO_2$ at 150 °C. Reaction conditions were the same as those of Figure 3: (○) NO; (□) N_2O; (●) adsorbed NO.

Another significant feature of the reactions at 150 °C was no formation of molecular nitrogen at the early stage of reaction, which became observable only after no nitric oxide existed in the gas phase, as clearly illustrated in Figure 4. Such a feature strongly suggests a successive transformation of NO → N_2O → N_2.

No production of ammonia in spite of the high activity of NO reduction on $CoTPP/TiO_2$ should be noted because unsupported CoTPP yielded a significant amount of the product at 200–250 °C.[4,15]

The catalytic activity of supporting titanium dioxide itself is shown in Table I where that of $CoTPP/TiO_2$ is also summarized for comparison. The support showed some activity; however, it was small enough at the temperatures examined to conclude that the excellent activity observed is ascribed to the binary catalyst of $CoTPP/TiO_2$. The catalyst showed the same activity in the repeated runs at 150 °C, suggesting its stable activity at that temperature.

Reactivity of nitric oxide on $CoTPP/TiO_2$ in the absence of hydrogen at 50 and 150 °C is summarized also in Table I. A small but distinct decomposition of nitric oxide to nitrous oxide over $CoTPP/TiO_2$ should be noted at 50 °C without hydrogen, although adsorption of nitric oxide was dominant for its consumption. Such a reaction has never been observed on unsupported CoTPP.[15] This reaction was further enhanced at 150 °C. The major product of this reaction was nitrous oxide. Nitrogen was a minor product especially at 50 °C, indicating its successive formation through nitrous oxide. Neither nitrogen dioxide nor oxygen was detected in the gas phase, suggesting the adsorption of oxygen in any form on the catalyst. Further analyses of the reaction are now in progress.

Such a significant enhancement of catalytic activity of CoTPP supported on TiO_2 may be explained in terms of the modified electronic structure of CoTPP described in the early part of this paper as well as the enlarged active surface of CoTPP. The partial reduction of cobalt ion may be favorable for its back-donation ability to produce an active species of anionic nitric oxide which may accelerate the adsorption and N-O bond cleavage of nitric oxide. The adsorption of hydrogen on $CoTPP/TiO_2$ which could never be observed on CoTPP alone may be related to the activation of hydrogen. This adsorption appears to be connected to the porphyrin ring because H_2TPP/TiO_2 could also adsorb hydrogen. Further study of the interaction of nitric oxide and hydrogen with supported CoTPP is now in progress.

In conclusion, the strong interaction of CoTPP and TiO_2 revealed in the present study may promise novel aspects of heterogeneous catalysis and photocatalysis.

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An Inelastic Electron Tunneling Spectroscopy Study of Some Iron Cyanide Complexes

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Inelastic electron tunneling spectroscopy is used to study the nature of the surface complex formed when several cyanide-containing iron complexes are adsorbed on freshly prepared alumina and hydrous alumina surfaces. The complexes studied are of the form $M_{(3,4)}Fe(CN)_5X$ where M = H, Li, Na, K, or Cs and X = CN^-, H_2O, or NO. Complexes are incorporated in tunnel diodes via adsorption from low concentration [10^{-8}–10^{-4} M] aqueous solutions. It is determined that complexes which contain iron(III) in solution are reduced to the plus two form in every case. Cation effects on the vibrational spectra observed indicate that charge compensation occurs by adsorption of the complex plus the requisit number of cations to form a relatively discrete surface unit. Computer fitting of the current-voltage characteristics of these doped diodes clearly shows that submonolayer adsorption is being studied. Further, by comparison of the barrier parameters with the tunneling spectra observed, a coherent picture of the nature of the adsorbed species is obtained. The tunnel diode structures used in this study are of the form $Al-Al_2O_3-M'$, where M′ = Pb, Sn, or Ag. Effects due to diffusion of Sn and Ag into the oxide layer on the vibrational spectra of the adsorbed layer ions are observed.

Introduction

Improved understanding of metal complexes as adsorbates on oxide and hydrous oxide surfaces is critical to many problems in surface chemistry. Such diverse topics as oxide-supported catalysts, surface-induced charge-transfer processes, and transport of metal-containing pollutants in natural waters will benefit from a thorough understanding of the nature of metal complexes on surfaces. Although a large body of literature relating to the stoichiometry and thermodynamics of metal complex adsorption on oxide surfaces exists,[1-5] little spectroscopic information is available. ESR spectroscopy has been shown to be useful for ellucidating the site symmetry of adsorbed paramagnetic ions,[6-8] however, it provides little other information about the nature of the adsorbed species and is inappropriate for diamagnetic complexes. The venerable infrared method is useless in the metal-ligand region of the spectrum due to the opacity of the substrates.[9-11] Raman spectroscopy provides a wider free spectral range for observing vibrational states of asorbed

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