One remaining point is the variation of the C–O stretch with the halide; the observed order ($I^- > Br^- > Cl^-$) follows the acidity order of the halides in the hydrohalic acids, except for F^-, which showed an anomalously large shift. This suggests an additional covalent interaction with F^- not present with the heavier halogens, as might be expected from the unique chemistry of the fluoride anion. A similar order of perturbation was noted for the CH_2 symmetric stretch and the CH_2 in-plane deformation modes, the two vibrations anticipated to be perturbed most significantly by the type of interaction proposed here.

In conclusion, the codeposition and reaction of alkali halide molecules with formaldehyde in argon matrices did not give rise to the expected halide anion transfer and formation of the CH_2XO^- anion. Rather, an unusual ion–dipole interaction was indicated between the halide anion and the carbon center of CH_2O, although in the case of CsF slight indication of a covalent interaction was noted. Theoretical studies of this system, including the alkali-metal cation, would be useful to fully characterize the nature of the interaction observed here.

Acknowledgment. The authors gratefully acknowledge support of this research by the National Science Foundation under Grant CHE8400450. B.S.A. also gratefully acknowledges the Dreyfus Foundation for a Teacher-Scholar Grant.

Registry No. CsF, 13400-13-0; CsCl, 7647-17-8; CsBr, 7787-69-1; CsI, 7789-17-5; RbI, 7790-29-6; KI, 7681-11-0; KBr, 7758-02-3; KCl, 7447-40-7; formaldehyde, 50-00-0.

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Infrared Study of Sulfur-Containing Iron Oxide. Behavior of Sulfur during Reduction and Oxidation

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When an SO_4^{2-} ion was introduced from $(NH_4)_2SO_4$ or H_2SO_4 onto Fe_2O_3, the resulting catalysts exhibited pronounced catalytic activities for acid-catalyzed reactions such as the ring-opening isomerization of cyclopropane, the dehydration of 2-butanol, and the skeletal isomerization of *n*-butane[1-3] on the one hand and were quite effective for a coal liquefaction[4] on the other. Though the oxidation state of sulfur in the former was believed to be S^{6+} and the electrophilic property of the S=O bond accounted for the enhanced acidic properties,[2] the role and the active state of S in the latter are still unknown, since the reaction is usually carried out under a high pressure of hydrogen and at high temperature and the introduced SO_4^{2-} ion could be reduced to lower oxidation states. This report deals with the influences of the source of sulfur and of the successive treatment on the oxidation states of the sulfur introduced. IR spectroscopic investigations were performed on the iron oxide treated with H_2S, SO_2, and $(NH_4)_2SO_4$ under oxidized conditions, and XPS measurements were employed to examine the states of sulfur under reduced conditions.

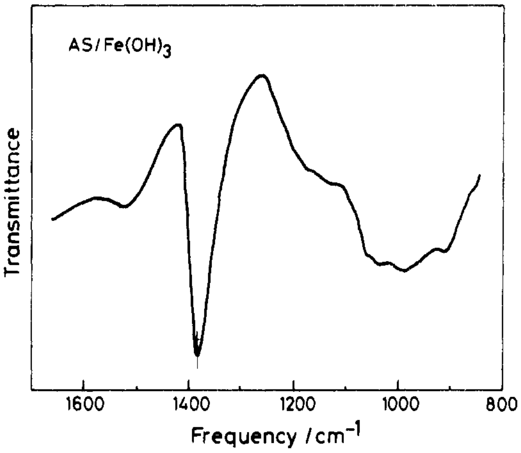

Figure 1. IR spectrum of $AS/Fe(OH)_3$ calcined at 500 °C.

Experimental Section

Iron hydroxide ($Fe(OH)_3$) was prepared by treatment of an aqueous solution of $Fe(NO_3)_3$ with aqueous ammonia (final pH 8–9), followed by washing and drying of the product at 100 °C. The sulfur-promoted catalysts were prepared by introducing inorganic sulfur compounds onto the hydroxide or the hydroxide calcined at 300 °C, followed by various treatments such as calcination, reduction, and oxidation. The $(NH_4)_2SO_4$-impregnated catalysts ($AS/Fe(OH)_3$) were prepared by immersing $Fe(OH)_3$ in an aqueous solution of ammonium sulfate, followed by calcining at 500 °C. The amount of sulfur loading was adjusted to ca. 2 wt % as SO_3. The H_2S-treated catalysts ($Fe(OH)_3$–H_2S) and SO_2-treated catalysts ($Fe(OH)_3$–SO_2) were obtained by treating $Fe(OH)_3$ with 9 torr of H_2S and SO_2 at desired temperatures. Starting materials and treating reagents are denoted as Fe_2O_3–H_2S etc.

The IR spectra of self-supported disks were recorded on a JASCO DS-701G infrared spectrometer at room temperature. Prior to the measurement, the samples were oxidized with O_2 at 350 °C for 10 min and evacuated at 350 °C, if necessary. The oxidation process was necessary to avoid low transmittance of samples.

X-ray photoelectron spectroscopy was performed on a VG ESCA 3 spectrometer. A reduction by H_2 and an oxidation by O_2 were carried out in a preparation chamber connected to the spectrometer. An H_2S treatment was performed in a separate vacuum manifold.

Results and Discussion

An $AS/Fe(OH)_3$ sample gave an intense band at 1370 cm^{-1} after evacuation above 300 °C (Figure 1). The changes of the ν_{SO} spectra from the hydrated $AS/Fe(OH)_3$ in the ν_1 and ν_3 region (900–1400 cm^{-1}) upon evacuation have been reported previously.[2] These spectra indicated a species of reduced C_{2v} symmetry with four bands (1240, 1140, 1025, and 924 cm^{-1}) arising from ν_1 and splitting of the triply degenerated ν_3 vibration. Upon evacuation, another set of absorptions appeared at 1340, 1140, 1015, and 915 cm^{-1}. The vibrations giving frequencies at 1340 and 1140 cm^{-1} are mainly associated with the free $>SO_2$ group, and the vibrations giving frequencies at 1015 and 915 cm^{-1} are mainly from the S–O vibrations of the $S(O-)_2$ group. Further evacuation above 100 °C resulted in a marked increase in intensity of the 1340-cm^{-1} band and a shift to 1370 cm^{-1}. Thus the band at 1370 cm^{-1} has been assigned to the asymmetric vibration of S=O bonds of the $O_2S(O-)_2$ species.[2] This assignment is supported by the spectra of organic covalent sulfates[5] (RSO_2R), which show absorption

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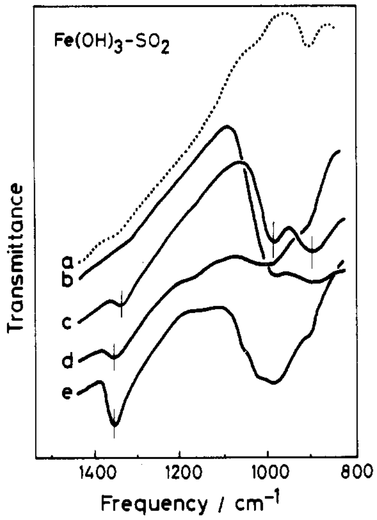

Figure 2. IR spectra of $Fe(OH)_3$ treated by SO_2: (a) background; (b) SO_2 adsorbed at room temperature, followed by evacuation at room temperature; (c) SO_2 adsorbed at 200 °C, followed by evacuation at 200 °C; (d) SO_2 admitted at 300 °C, followed by evacuation at 300 °C; (e) sample from step d after O_2 was admitted at 300 °C, followed by evacuation at 300 °C.

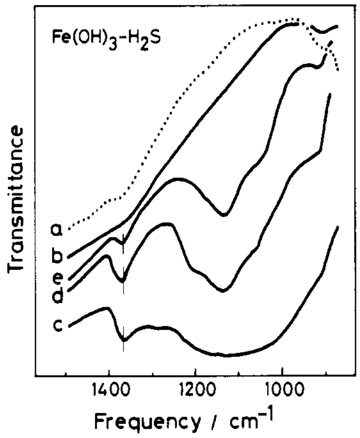

Figure 3. IR spectra of $Fe(OH)_3$ treated by H_2S: (a) background; (b) H_2S adsorbed at room temperature; (c) H_2S adsorbed at 200 °C, followed by oxidation at 200 °C; (d) H_2S adsorbed at 400 °C, followed by oxidation at 400 °C; (e) H_2S adsorbed at 500 °C, followed by oxidation at 500 °C.

near 1230–1150 and 1440–1350 cm^{-1}. The S=O stretching vibration of SO_4^{2-} in metal sulfates usually lies around 1235–1100 cm^{-1}.

The adsorption of SO_2 at room temperature on $Fe(OH)_3$ calcined at 300 °C gave a broad band at 1000–800 cm^{-1} after evacuation at room temperature (Figure 2). When the evacuation temperature was raised to 200 °C, this band decreased in intensity and split into two bands at 985 and 900 cm^{-1} and a 1340-cm^{-1} band was observed. The former bands were assigned to the stretching frequencies of SO_3^{2-} species. Oxygen-bonded sulfito species such as $Tl_2[Cu(SO_3)_2]$ give 902- and 862-cm^{-1} (ν_3) and 989-cm^{-1} (ν_1) bands.[6] Evacuation at 300 °C and the admission of O_2 gas gave spectrum e in Figure 2, in which formation of $>SO_2$ species is clearly demonstrated by the asymmetric stretching frequency of S=O bonds (1370 cm^{-1}). A part of the large absorption at around 1000 cm^{-1} could be assigned to the absorption of a symmetric stretching frequency of S=O bonds; a mixture of SO_3^{2-} and SO_4^{2-} species may also be involved.

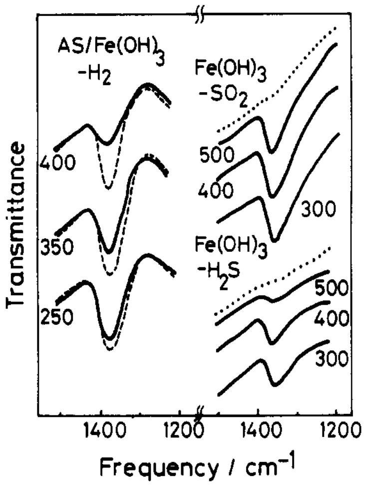

Figure 4. Changes of IR spectra of $AS/Fe(OH)_3$ and $Fe(OH)_3$ after various treatments. Values indicate treatment temperatures. All the spectra were obtained after O_2 oxidation at 500 °C. Broken lines indicate the spectra before H_2 treatments. Dotted lines indicate the spectra before SO_2 or H_2S adsorption.

The admission of H_2S at 200 °C onto $Fe(OH)_3$ dried at 100 °C and successive oxidation followed by evacuation at the same temperature gave a 1370-cm^{-1} band and a broad band around 1100 cm^{-1} (Figure 3), which indicate the formation of $>SO_2$ and SO_4^{2-} species, respectively.[2,6] Adsorption of H_2S at 400 °C, followed by oxidation at the same temperature gave a well-isolated 1370-cm^{-1} band. The broad band around 1100 cm^{-1} lost its intensity slightly.

Figure 4 summarizes the spectral changes during the processes of reduction–oxidation of $AS/Fe(OH)_3$, H_2S adsorption–oxidation of $Fe(OH)_3$, and the adsorption of SO_2 on $Fe(OH)_3$. The intensities of the 1370-cm^{-1} band in the SO_2-treated samples were kept almost constant after reoxidation, whatever the temperature of SO_2 adsorption was. This suggests that SO_2 interacted with the surface at any temperature is easily oxidized to $>SO_2$ with oxygen treatment. In the cases of $AS/Fe(OH)_3$ reduced with H_2 and $Fe(OH)_3$ treated with H_2S at lower temperatures, the oxygen treatment was also effective to recover the intensity of the 1370-cm^{-1} band. However, the intensity decreased when $AS/Fe(OH)_3$ and $Fe(OH)_3$ reduced with H_2 and treated with H_2S, respectively, at higher temperatures were oxidized with oxygen. The loss in intensity after the reduction–oxidation process may be due to two reasons: a loss of sulfur during the reduction–oxidation process and/or the difficulty in the oxidation of highly reduced states of sulfur such as S^{2-} as sulfides. The former could arise under such conditions where the sample was reduced deeply to form metallic particles partially, and the following oxidation gave rise to a highly exothermic process to give a temperature above 700 °C. A loss of sulfur as gaseous SO_3 above 700 °C was confirmed by a DTA–TG measurement. Since the oxidation and reduction between S^{6+} and S^{2-} were reversible, which was revealed by XPS measurements, the latter seems unlikely. Figure 5 illustrates the changes in the S 2p signals of $AS/Fe(OH)_3$ and $Fe(OH)_3$–H_2S. When $AS/Fe(OH)_3$ was reduced in situ by a few torr of H_2 at 450 °C, the intensity of the S 2p signal of S^{2-} increased and that of S^{6+} decreased. H_2S treatment of $Fe(OH)_3$ calcined at 500 °C gave only one signal, which indicates the presence of the S^{2-} state. In situ oxidation of both samples by a few torr of O_2 at 300 °C resulted in the complete oxidation from the S^{2-} to S^{6+} state.

Thus, it is concluded that the introduction of sulfur from SO_2, H_2S, and $(NH_4)_2SO_4$ leads to the formation of $>SO_2$ species after the oxidation and even the reduced state of sulfur

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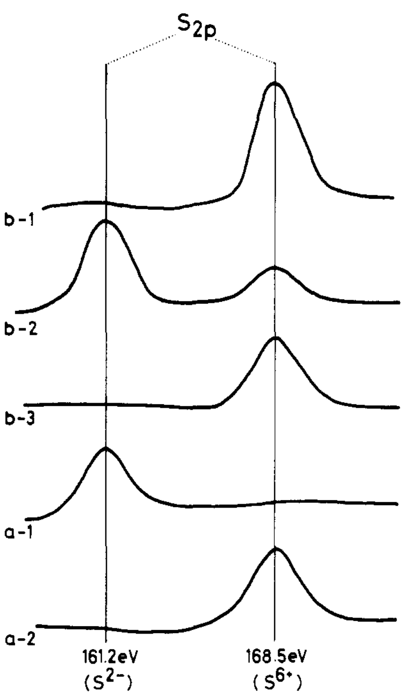

Figure 5. Changes in S 2p signals by reduction and oxidation for the following samples: (a-1) $Fe(OH)_3$ treated by a few torr of H_2S at 500 °C; (a-2) sample a-1 oxidized in situ by a few torr of O_2 at 500 °C; (b-1) $AS/Fe(OH)_3$ calcined at 500 °C, followed by evacuation in situ at 500 °C; (b-2) sample b-1 reduced in situ by a few torr of H_2 at 450 °C; (b-3) sample b-1 oxidized in situ by a few torr of O_2 at 300 °C.

can be oxidized to the $>SO_2$ state.

Acknowledgment. The present work was supported by a Grant-in-Aid for Special Research (No. 57040002) of the Ministry of Education, Science and Culture, Japan. We thank Prof. I. Toyoshima and Dr. Ka. Tanaka of the Research Institute for Catalysis, Hokkaido University, for their cooperation in XPS experiments.

Registry No. S, 7704-34-9; H_2S, 7783-06-4; SO_2, 7446-09-5; $(NH_4)_2SO_4$, 7783-20-2; $Fe(OH)_3$, 1309-33-7; Fe_2O_3, 1309-37-1.

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N-Acyl Isocyanide Complexes of Iron(II) Porphyrins. Access to Mixed-Ligand Species Using a Substitute for Carbon Monoxide

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Scheme I

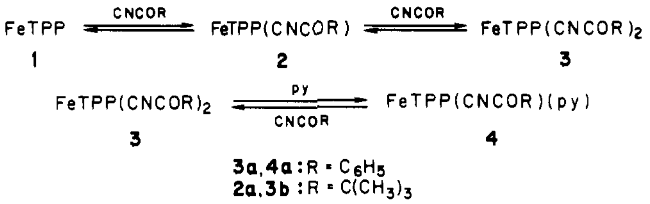

Table I. Carbonyl and Isocyanide Stretching Frequencies of FeTPP Complexes[a]

L	free ligand	$FeTPP(L)_2$	FeTPP(L)	FeTPP(L)(py)
$\nu(CO)$	2143	2042[b]	1973[b]	1980[c]
$\nu(CNCOC_6H_5)$	2100[d]	2040		1980
$\nu(CNCOC(CH_3)_3)$	2100[d]	2045	1970	
$\nu(CNC(CH_3)_3)$	2130	2129[e]		

[a] Nujol. [b] From ref 6. [c] From ref 14. [d] From ref 9. [e] From ref 7.

Table II. Mössbauer Data for Substituted Iron(II) Tetraphenylporphyrins at 298 K

compd	δ[a]	ΔE_Q[b]	Γ[c]
$FeTPP(CNCOC_6H_5)_2$	0.16	0.26	0.26
$FeTPP(CO)_2$[d]	0.19	0.27	0.26
FeTPP(CNCOPh)(py)	0.19	0.58	0.25
FeTPP(CO)(pip)[e]	0.18	0.53	0.24

[a] Isomer shift in mm/s relative to iron; ±0.01 mm/s. [b] Quadrupole splitting; ±0.02 mm/s. [c] Line width in mm/s at half-maximum. [d] Reference 15. [e] Reference 16.

Although isocyanides (CNR) are not natural substrates in biological systems, their interactions with hemoproteins have been extensively studied.[1] The interest in isocyanides derives from a possible understanding of the steric effect of R on rates and equilibria of binding in human hemoglobin. Particularly significant results have recently been reported for both the protein[2] and porphyrin models[3] using classical alkyl isocyanides in solution. Previously, we described *N*-acyl isocyanide complexes of chromium(0).[4] The synthetic and spectroscopic results observed with electron-deficient isocyanides revealed ligand properties similar to those of carbon monoxide. This behavior prompts us to consider the application of the CNCOR group as a substrate in porphyrin chemistry. We report here the preparation of FeTPP(CNCOR), $FeTPP(CNCOR)_2$, and FeTPP(CNCOR)(base) (R = C_6H_5, $(CH_3)_3C$; base = pyridine, 1-methylimidazole, 4-cyanopyridine).[5] The spectral properties of these new complexes are discussed in comparison with those of carbon monoxide[6] and alkyl isocyanide adducts.[7]

Results and Discussion

Our results are summarized in Scheme I. Treating FeTPP (**1**)[8] with 2 equiv of *N*-benzoyl isocyanide[9] in CH_2Cl_2 at -40 °C followed by addition of methanol yields the purple crystalline complex **3a** in 85% yield. The position and shape of the signals in its ^1H NMR spectrum (-40 °C, $CDCl_3$, $SiMe_4$), 8.78 (s, 8 H), 7.97 (m, 8 H), and 7.43 ppm (m, 12 H) for the protons of the porphyrin ring and 7.15 (m, 4 H) and 6.81 ppm (m, 6 H) for the protons of $CNCOC_6H_5$, are indicative of low-spin iron(II). The electronic spectrum of this new derivative exhibits λ_{max} at 428 nm (ϵ 4.30 × 10^5), 553 nm (ϵ 1.07 × 10^4), and 593 nm (ϵ 6.16 × 10^3) in toluene. Mössbauer and IR spectra confirm the structure (see Tables I and II). Moreover, it is interesting to note that, by use of *N*-pivaloyl

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