Removal of NO$_x$ with cobalt phthalocyanine supported on Y-type faujasite and alumina

Keiji Hashimoto[*], Naoji Toukai

Osaka Municipal Technical Research Institute, Morinomiya, Joto-ku, Osaka 536-8553, Japan

Abstract

The oxidative removal of NO with oxygen over a catalyst consisting of β-form cobalt phthalocyanine supported on SiO$_2$, TiO$_2$, Y-type faujasite, and alumina was studied at 30 °C. The order of NO$_x$ adsorption capacity is as follows: Co-Phc/Al$_2$O$_3$ > Co-Phc/YZ ≫ YZ > Al$_2$O$_3$ > Co-Phc/SiO$_2$, Co-Phc/TiO$_2$, SiO$_2$, TiO$_2$ ≒ 0 > Co-Phc(β) = 0. The catalysts, Co-Phc/YZ and Co-Phc/Al$_2$O$_3$, were regenerated by water washing and could be used again. Infrared spectra for Co-Phc/YZ and Co-Phc/Al$_2$O$_3$ indicate that the removed NO$_x$ exists in the catalyst surface as adsorption species of NO, NO$_2$ and NO$_3{}^-$. The superhyperfine structures of ESR spectra for Co-Phc/YZ and Co-Phc/Al$_2$O$_3$ support that the Co–N bonding occurs on admitting a mixture gas of oxygen (10 Pa) and NO (0.2 Pa). Therefore, it is concluded that the β-form cobalt phthalocyanine supported on alumina and Y-type faujasite is effective for the oxidative removal of NO at 30 °C.
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Keywords: Oxidative removal of NO; Cobalt-phthalocyanine; Y-type faujasite; Alumina

1. Introduction

The worsening of one's living environment due to NO$_x$ has constituted a serious social problem. It is very difficult to remove dilute NO$_x$ gas which has been exhausted into an atmosphere from motor cars and manufactories. The photocatalytic oxidation using solar energy for the oxidation of NO has been recently noticed as a reasonable key technology to resolve the difficult problem. However, the photocatalytic technology using sunlight energy should be inefficient at night and in broken weather. Therefore, it is desirable for a practical use that photoenergy is nonessential to removal of the dilute NO$_x$ from an atmosphere. It is well-known that metal phthalocyanates are often effective for the oxidation of organic compounds with

oxygen in mild conditions [1–5]. In addition, metal phthalocyanates are generally insoluble in water. The insolubility is important for a practical use, because the insoluble catalytic materials possibly avoid deactivation resulting from dissolution in rainy water and a water washing is possible to regenerate the used catalyst. We have studied on the development of an environmental catalyst that is useful for the removal of NO$_x$ [6,7]. We have already reported that a titania prepared by high-temperature hydrolysis of titanium tetra-alkoxides in hydrocarbon solvent is very active for photocatalytic removal of NO [6] and the composite catalysts of the titania and zeolites are also very effective [7]. We attempted to apply metallophthalocyanines to the oxidative removal of NO. We found that β-form cobalt phthalocyanine supported on alumina and zeolite is effective for the oxidative removal of the dilute concentration of NO to NO$_2$ with oxygen.

* Corresponding author.

In this paper, we report (1) efficiency of β-form cobalt phthalocyanine loaded on Al_2O_3 and Y-type faujasite; (2) formation of Co–NO_x bond between NO_x and cobalt phthalocyanine; (3) adsorption species of NO_x on the catalysts.

2. Experiment

2.1. Materials

Pyridine (analytical grade), silica and titania (anatase form, Ishihara Sangyou Co.) and β-form cobalt phthalocyanine (dye content 97%, Aldrich Chem. Co.) were commercial reagents and used without further purification. NO gas (2.0 ppm, He balance, Takachiho Kagaku Kogyo Co.) was used. Y-type faujasite (Z-HY5.6) and γ-alumina (JRC-AlO-4) were supplied by the Catalysis Reference Committee of the Japan Catalysis Society.

2.2. Preparation of β-form cobalt phthalocyanine loaded on a support, Y-type faujasite (Co-Phc/YZ), alumina (Co-Phc/Al₂O₃), silica (Co-Phc/SiO₂), and titania (Co-Phc/TiO₂)

β-Form cobalt phthalocyanine loaded on a support was prepared by an impregnation method; in a typical preparation, 2 g of a powder support such as proton form Y-faujasite, alumina, silica and titania was impregnated in 8.0 ml of pyridine solution containing 0.050 g of β-form cobalt phthalocyanine and then the solvent was evaporated. The resulting blue powder was dried at 150 °C for 5 h.

2.3. Oxidative removal of NO

The oxidative removal of NO was carried out in a fixed bed continuous flow tubular reactor: the reactor was made of a 3-mm i.d. pyrex-glass. The catalyst, 0.060 g, was sandwiched with quartz wool in the reactor. At first, an air stream (partial pressure of oxygen, 10 kPa) containing 1–1.5 ppm of NO at a flow rate of 60 ml min^{-1} was passed through the by-path of the reactor and the gas-flow line attained an equilibrium adsorption of NO. The reaction mixture gas was then passed through the reactor. The measurement of NO_x removal was carried out at 30 °C under an atmospheric

pressure. The concentrations of NO and NO_2 in the reaction gas were analyzed on-line at an interval of 3 min by a Yanaco ECL-880US NO_x meter. The concentrations of NO and NO_2 in a feed reaction gas were determined by sampling at an entrance of the flow reactor before and after reaction. The concentration of NO_2 was very low, 0.01 ppm, in the feed gas, because NO gas was mixed into the air stream just before the reactor and NO concentration is low, 1–1.5 ppm, in the feed gas. The amount of the oxidative removal was determined from the difference between a concentration of NO_x in the feed gas and that in the out-let gas: a concentration of NO_x represents the sum of NO and NO_2 concentrations, though the NO_2 concentration is negligible. The pyrex-glass reactor and quartz wool (packing material) make no contribution to the oxidation.

2.4. Surface area

Surface area was determined by the BET method using nitrogen adsorption at −196 °C.

2.5. X-ray powder diffraction (XRD) analysis

XRD patterns of the samples were recorded using a Mc-Science XP$_{18}$ spectrometer (Ni-filtered Cu Kα, 40 kV, 80 mA). The sample was mounted on a sample board and the measurements were carried out immediately.

2.6. FT-IR measurements

The FT-IR spectra were recorded by a Shimadzu FT-IR 8100 using a conventional IR cell connected to a vacuum line and adsorption apparatus. The sample (0.01 g) was pressed at 7.5 t/cm^2 using a pellet die to form a wafer with 10-mm diameter and then placed into the in situ IR cell which allowed heating under vacuum. After the wafer was heated in vacuo for 2 h, FT-IR spectra for the degassed sample were measured as a reference spectrum. The wafer was exposed to NO gas (0.1 kPa) at room temperature. FT-IR spectra for the sample of NO adsorption were recorded at room temperature prior to admittance of oxygen (1.0 kPa). FT-IR spectra were then recorded in the presence of a mixture gas of oxygen and NO.

2.7. ESR measurements

ESR spectra were recorded on a Japan Electron ESR analyzer using a conventional ESR tube connected to a vacuum line and adsorption apparatus. The ESR tube equipped with a vacuum cock was made of pyrex-glass with 3-mm diameter. The Co-Phc/YZ (200 mg) was packed in the ESR tube and treated in vacuo at 300 °C for 2 h. ESR spectra for the degassed Co-Phc/YZ were recorded at -150 °C as a reference spectrum. ESR spectra for adsorption species of NO_x were also recorded at -150 °C in the presence of oxygen and NO. Manganese marker was used as a standard. The ESR measurements for Co-Phc/Al_2O_3 were similarly carried out according to the procedures described earlier.

3. Result and discussion

The oxidative removal of NO over YZ, Al_2O_3, SiO_2, TiO_2, Co-Phc(β), Co-Phc/YZ, Co-Phc/Al_2O_3, Co-Phc/TiO_2 and Co-Phc/SiO_2 was studied at 30 °C. The removal ratio of NO_x for 1 h was summarized in Table 1. The Co-Phc/YZ and Co-Phc/Al_2O_3 are effective for the oxidative removal, whereas the amount of NO_x removal with Co-Phc/SiO_2, Co-Phc/TiO_2, Co-Phc(β), YZ, Al_2O_3, SiO_2, and TiO_2 are negligible in the oxidative removal, although these slightly adsorb NO_x gas only in an initial reaction period. These results indicate that the load of Co-Phc on YZ

Table 1
Removal of NO_x over Co-Phc catalysts

Catalyst	Removal ratio of NO_x (%)	
	30 °C	50 °C
Co-Phc/Al_2O_3	92	98
Co-Phc/YZ	81	85
Co-Phc/SiO_2	Negligible	Negligible
Co-Phc/TiO_2	Negligible	Negligible
β-Co-Phc	None	None
YZ	6	5
Al_2O_3	2	2
SiO_2	Negligible	Negligible
TiO_2	Negligible	Negligible

Catalyst 0.060 g; NO 1 ppm; air balance, SV 60000 h^{-1}; reaction temperature 30 and 50 °C; reaction time 1 h; removal ratio = ratio of removal amount of NO_x to amount of NO_x feed.
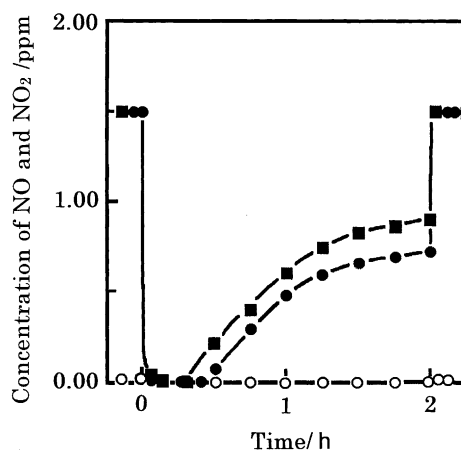

Fig. 1. Time-on-stream in the variation of NO and NO_2 concentration for the oxidative removal using Co-Phc/YZ and Co-Phc/Al_2O_3. NO concentration in feed gas: 1.50 ppm; air balance, flow rate, 60 ml/min; catalyst, 60 mg; SV, 60000 h^{-1}; reaction time, 2 h; reaction temperature, 30 °C; (●) NO concentration in the treatment with Co-Phc/Al_2O_3, (■) NO concentration in the treatment with Co-Phc/YZ, (○) NO_2 concentration in the treatment with Co-Phc/YZ or Co-Phc/Al_2O_3.

and Al_2O_3 significantly increases the adsorption capacity of NO_x. The time-on-stream variation in the concentrations of NO and NO_2 was studied on the oxidative removal over Co-Phc/YZ and Co-Phc/Al_2O_3. The results are shown in Fig. 1. The most of NO is adsorbed on the catalysts in an initial period of the reaction. The concentration of NO in the out-let gas increases with an increase in reaction time, i.e. the amount of the removal decreases gradually, while the concentration of NO_2 in the out-let gas is negligible for 2 h under the reaction conditions. The mixture gas of NO and NO_2 is desorbed on heating the used catalysts, though the feed gas scarcely contains NO_2 (0.01 ppm): the amount of the desorbed NO_2 is larger than that integrated the concentration of NO_2 in the feed gas. The results indicate that the oxidation of NO to NO_2 over Co-Phc/YZ and Co-Phc/Al_2O_3 proceeds at 30 °C and the formed NO_2 adsorbs on the catalysts. Furthermore, the catalysts, Co-Phc/Al_2O_3 and Co-Phc/YZ, were regenerated by water washing, and could be used again for the NO_x removal.

The BET surface area of the catalysts were measured by using nitrogen adsorption at liquid nitrogen and summarized in Table 2. The load of cobalt phthalocyanine on Y-type faujasite decreases significantly the

Table 2
Surface area of the catalyst

Catalyst	Surface area (m^2/g)
Co-Phc/Al$_2$O$_3$	181
Co-Phc/YZ	250[a]
Co-Phc/SiO$_2$	586
Co-Phc/TiO$_2$	54

[a] Calculated conveniently from the amount of saturation adsorption of nitrogen at $-196\,^\circ$C.

saturation adsorption of nitrogen on the zeolite. The load of cobalt phthalocyanine on the faujasite should be caused to block and/or fill the cavities. The decrease in the saturation adsorption probably makes some contributions to less activation of Co-Phc/YZ, compared with Co-Phc/Al$_2$O$_3$. However, the removal efficiency of NO$_x$ dose not always depend on the surface area.

X-ray diffraction patterns for the Co-Phc/YZ were recorded and shown in Fig. 2. The patterns are well consistent with those for Y-type faujasite used as a support. The structure of Y-type faujasite is preserved in the Co-Phc/YZ.

FT-IR spectra for the Co-Phc/YZ and Co-Phc/Al$_2$O$_3$ were measured and shown in Fig. 3. In the range of 2000–1000 cm^{-1}, the Co-Phc/YZ gives the IR vibration bands at 1584, 1524, 1485, 1472, 1428, 1335, and 1291 cm^{-1} and Co-Phc/Al$_2$O$_3$ gives ones at 1592, 1572 cm^{-1} (with a shoulder at 1560 cm^{-1}), 1526, 1485, 1472, 1447, 1428, 1402, 1366, 1333, 1291, 1266, 1231, 1196, 1165, 1123, 1094, 1076, 1032 and 997 cm^{-1}. In the literature [8], β-form cobalt phthalocyanine exhibits sharp stretching bands at 1611, 1524, 1470, 1426, 1333, 1291, 1165 cm^{-1} (with a shoulder at 1173 cm^{-1}), 1121, 1090, 1076 cm^{-1} (with a shoulder at 1064 cm^{-1}) and weak bands at 1725, 1595, 1541, 1491, 1375, 1202 and 1001 cm^{-1}: the bands at 1611, 1595, and 1491, 1001 cm^{-1} are assigned to
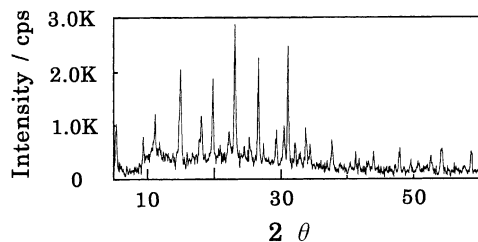
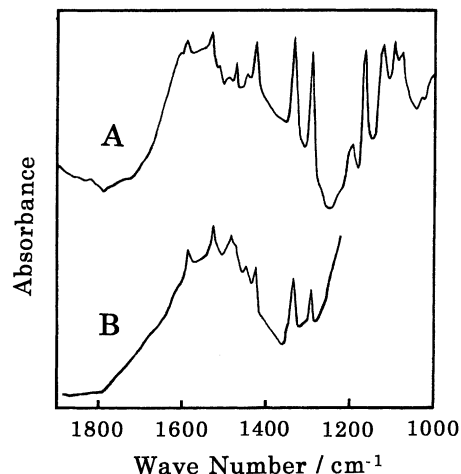Fig. 2. X-ray diffraction patterns of Co-Phc/YZ.

Fig. 3. FT-IR spectra of the catalysts. (A) Co-Phc/Al$_2$O$_3$, (B) Co-Phc/YZ. The catalysts were evacuated at 300 $^\circ$C for 2 h.

stretching vibration of C–C bond in benzene ring of phthalocyanine; the bands at 1370, 1165, 1120, and 1076 cm^{-1} are assigned to stretching vibration of C–H in phthalocyanine and the band at 1090 cm^{-1} is assigned to C–N stretching mode from pyrrole dominate. The Infrared spectra for the Co-Phc/YZ and Co-Phc/Al$_2$O$_3$ display the characteristic stretching vibrations of C–C, C–H and C–N bonds in cobalt phthalocyanine, though each bands are slightly shifted and/or their strengths change. In particular, the bands at 1165, 1120 and 1076 cm^{-1} in Co-Phc/Al$_2$O$_3$ clearly indicate the existence of β-form cobalt phthalocyanine on the alumina, because these bands are characteristics of β-form cobalt phthalocyanine [8]. The results, hence, lead to the conclusion that cobalt phthalocyanine is supported on the Y-type faujasite and alumina.

FT-IR spectra of NO adsorbed on the Co-Phc/YZ and Co-Phc/Al$_2$O$_3$ were recorded and shown in Fig. 4. The spectrum for the Co-Phc/YZ displays the bands at 1734, 1584, 1516, 1485, 1447, 1385 and 1264 cm^{-1} in the presence of NO and oxygen, whereas that displays the bands at 1896 and 1809 cm^{-1} in the absence of oxygen. The admittance of NO and oxygen causes an IR spectrum including the bands at 1748, 1584 cm^{-1} (with a shoulder around 1600 cm^{-1}), 1516, 1485, 1383, and 1252 cm^{-1} in Co-Phc/Al$_2$O$_3$. In the literatures [9–11], the adsorption of NO on cobalt ions supported on zeolites exhibits asymmet-
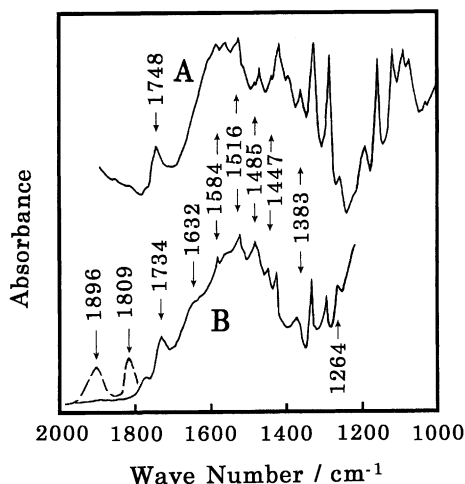
Fig. 4. FT-IR spectra of NO_x species on Co-Phc/YZ and Co-Phc/Al_2O_3. The catalysts were exposed at room temperature to a mixture gas of 1 kPa of O_2 and 0.1 kPa of NO. Dotted line: exposure to NO in the absence of oxygen; (A) Co-Phc/Al_2O_3; (B) Co-Phc/YZ.

ric stretching band at 1800–1820 cm^{-1}, symmetric band at 1890–1935 cm^{-1}: the stretching vibration of mononitrosyls occurs at 1800, 1886–1890 and 1928–1935 cm^{-1}; the mononitrosyls bands are unstable at room temperature. Moreover, the asymmetric stretching mode of dinitrosyl species, Co(NO)$_2$, displays the bands at 1810 cm^{-1} for Co-mordenite and Co-MFI, and 1821 cm^{-1} for Co-faujasite [12] and the asymmetric stretching bands of dinitrosyl species over Co/Al_2O_3 occurs in the region of 1780–1796 cm^{-1} [13]; the asymmetric one over Cu-MFI occurs at 1734 cm^{-1} [14]. IR absorption, arising from asymmetric and symmetric vibrations of nitro complexes, occurs in the general region around 1650–1250 and 1350–1250 cm^{-1}, respectively, whereas IR absorption, arising from those of unidentate nitrato complexes, occurs in the region of 1522–1420 and 1305–1250 cm^{-1}, respectively [15]. The bands at 1896 and 1809 cm^{-1} are attributed to the symmetric and asymmetric stretching vibration of dinitrosyls on the zeolite, because the bands are stable at room temperature and disappear on admitting oxygen. Although the band at 1734 cm^{-1} remains on admitting oxygen, the band is believed to be attributable to the asymmetric stretching of dinitrosyl species on the different adsorption sites of the zeolite. The band

at 1748 cm^{-1} is similarly attributable to the asymmetric stretching of dinitrosyl species on the Al_2O_3. The bands at 1584, 1516, 1485, 1447, 1385 and 1264 cm^{-1} for Co-Phc/YZ and at 1584 cm^{-1} (with a shoulder around 1600 cm^{-1}), 1516, 1485, 1383, and 1252 cm^{-1} for Co-Phc/Al_2O_3 are attributed to the asymmetric and symmetric vibrations of nitro species and/or nitrato ones. These results indicate that adsorption species on Co-Phc/YZ and Co-Phc/Al_2O_3 exist as dinitrosil, nitro and nitrato species.

ESR spectra for Co-Phc/YZ and Co-Phc/Al_2O_3 in the presence of NO (0.2 Pa) and oxygen (10 Pa) were measured and shown in Fig. 5. The spectra give a complex structure in the high magnetic field of 230–390 mT as shown in Fig. 5. In the literatures [16,17], the high and low-field structures of β-form cobalt phthalocyanine consist of eight split peaks, respectively; the low-field structure appears in the range of 140–300 mT and the high-field one in the range of 260–410 mT. Furthermore, the spectrum of β-form cobalt phthalocyanine treated in vacuo reveals a single sharp peak due to a free radical. As shown in Fig. 5, a strong single peak at $g = 2.003$ is observed and attributed to a free radical. The high-field set consists of
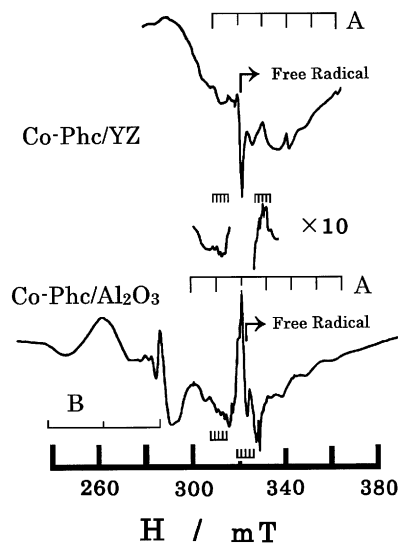

Fig. 5. ESR spectra of NO adsorbed on Co-Phc/YZ and Co-Phc/Al_2O_3 in the presence of oxygen. Pressure of NO, 0.2 Pa; Pressure of O_2, 10 Pa; (A) A value; (B) B value; unmarked; superhyperfine.

Table 3
Parameter of cobalt phthalocyanine

Catalyst	g-value	$g_{\parallel}$	$g_{\perp}$	HF (cm^{-1})	A (cm^{-1})	B (cm^{-1})
Co-Phc/YZ	–	1.92 ± 0.01	–	0.0015	0.0093	–
Co-Phc/Al$_2$O$_3$	2.58	1.91 ± 0.01	2.92 ± 0.02	0.0016	0.0097	0.033
β-Co-Phc[a]	2.374	2.029	2.546	None	0.0085	0.0096
β-Co-Phc[b]	2.57	1.89 ± 0.01	2.94 ± 0.01	None	0.015–6	0.028

[a] Sulfuric acid solution [16].
[b] Ref. [17]. HF, superhyperfine constant.

six visible peaks for Co-Phc/YZ, equally spaced with a separation of 10.4 mT in the region of 290–360 mT, whereas in Co-Phc/Al$_2$O$_3$, the low-field set consists of three visible peaks, equally spaced with a separation 24.0 mT and the high-field set consists of seven visible peaks, equally spaced with a separation 10.9 mT; the hyperfine coupling constant is determined to be $A = 0.0093\,cm^{-1}$ for Co-Phc/YZ, and $A = 0.0097$ and $B = 0.033\,cm^{-1}$ for Co-Phc/Al$_2$O$_3$. These hyperfine structures appear when β-form cobalt phthalocyanine is loaded on these supports. The ESR spectra are attributed to β-form cobalt phthalocyanine. These A values are slightly smaller than that, $0.015–6\,cm^{-1}$, reported for the high-field set of β-form cobalt phthalocyanine, whereas the B value for Co-Phc/Al$_2$O$_3$ is rather larger than that, 0.028, in the high-field set of β-form cobalt phthalocyanine; these A values nearly correspond to that for β-form cobalt phthalocyanine in sulfuric acid solution (Table 3). The result suggest that the A values perhaps depend on the acidity of proton form Y-type faujasite and alumina. A superhyperfine structure is not observed for Co-Phc/YZ and Co-Phc/Al$_2$O$_3$, but appears on admittance of the mixture gas of NO (0.2 Pa) and O$_2$ (10 Pa) to the catalysts. The amount of NO$_x$ adsorption under the pressure of NO (0.2 Pa) and O$_2$ (10 Pa) is <2% of the supported β-form cobalt phthalocyanine. In literature [22], the admolecule of NO$_2$ on zeolite gives g-tensor of $g_{xx} = 2.0048–55$, $g_{yy} = 1.9910–3$, $g_{zz} = 2.0008–2.0017$, $A_{xx} = 5.01–36$ mT, $A_{yy} = 4.58–4.80$ mT, and $A_{zz} = 6.55–6.97$ mT, whereas the admolecule of NO on zeolite gives g-tensor of $g_{xx} = 1.970–2.000$, $g_{yy} = 1.970–1.999$, and $g_{zz} = 1.79–1.95$. The more the pressure of NO and O$_2$ increases, the more amount of NO$_x$ adsorption increases. The amount of NO$_x$ adsorption under the pressure of O$_2$ (1 kPa)

and NO (0.1 kPa) is more than that of the supported β-form cobalt phthalocyanine. As a matter of course, the spectrum revealed a further complex structure which appeared to contain admixtures of a free radical, cobalt phthalocyanine and admolecules of NO and NO$_2$ on zeolite when admittance of O$_2$ (1 kPa) and NO (0.1 kPa) to Co-Phc/YZ. The superhyperfine structure should become obscure. A similar spectrum should be also observed for Co-Phc/Al$_2$O$_3$. The results support the idea that the superhyperfine structure is attributable to the complex of β-form cobalt phthalocyanine and NO$_x$. The superhyperfine structure similar to the observation was reported for the spectrum of cobalt phthalocyanine coordinated with heterocyclic amines [17]; the cobalt high-field hyperfine lines are split each into five superhyperfine lines owing to the magnetic interaction between the 3d electron and extra out-of-plane molecular nitrogen atoms. Moreover, no superhyperfine structure typical of the in-plane pyrrole nitrogens has been found as was the case with copper and cobalt phthalocyanine [17–20]. In fact, the superhyperfine structure dose not appear in Co-Phc/YZ and Co-Phc/Al$_2$O$_3$, but appears only in the coexistence of the rarefied NO$_x$, as described earlier. That the cobalt high-field hyperfine lines are split each into five superhyperfine lines is caused by the atoms (nuclear spin, $M_I = 1$) associated with the cobalt component. In this case, nitrogen atom only has $M_I = 1$. The admolecule of NO$_x$ on Co-Phc/YZ and Co-Phc/Al$_2$O$_3$ contains one nitrogen atom whose non-bonding orbital interacts with the Co^{2+} unpaired electron. The third and fifth cobalt high-field hyperfine lines for Co-Phc/YZ, and the second and third cobalt high-field hyperfine lines for Co-Phc/Al$_2$O$_3$ are well resolved and each is split into five superhyperfine lines as expected (Fig. 5). The superhyperfine coupling con-

stants are determined to be 0.0015 and 0.0016 cm^{-1} for Co-Phc/YZ and Co-Phc/Al$_2$O$_3$, respectively. The coupling constant is slightly larger or nearly equal in comparison to those, 0.0011–0.0016 cm^{-1}, for cobalt phthalocyanine dissolved in heterocyclic amines [17]. The internuclear distance of Co–NO$_2$ is estimated to be rather shorter or nearly equal in comparison to those of Co–heterocyclic amines such as Co–NC$_5$H$_5$: the internuclear distances of Co–NO$_2$ in nitro-amine–cobaltic complexes, 0.19–0.20 nm [21]; those of Co–heterocyclic amine in heterocyclic amine–cobalt phthalocyanine complexes, 0.21 nm [17]. The obtained value of the coupling constant is, hence, reasonable because the coupling constant is theoretically dependent on overlap between the cobalt and nitrogen orbitals. The results support the idea that the N–Co bond between nitrogen oxides and cobalt phthalocyanine forms.

4. Conclusion

The Co-Phc/YZ and Co-Phc/Al$_2$O$_3$ are effective for the oxidative removal, whereas the amount of NO$_x$ removal with Co-Phc/SiO$_2$, Co-Phc/TiO$_2$, Co-Phc(β), YZ, Al$_2$O$_3$, SiO$_2$, and TiO$_2$ are negligible in the oxidative removal. The order of NO$_x$ adsorption capacity is as follows; Co-Phc/Al$_2$O$_3$ > Co-Phc/YZ $\gg$ YZ > Al$_2$O$_3$ > Co-Phc/SiO$_2$, Co-Phc/TiO$_2$, SiO$_2$, and TiO$_2$ $\doteqdot$ 0 > Co-Phc(β) = 0. Infrared spectra for Co-Phc/YZ and Co-Phc/Al$_2$O$_3$ when admitting NO and oxygen exhibit the bands due to the oxidation products of NO such as NO$_2$ and NO$_3^-$. The mixture gas of NO and NO$_2$ is desorbed on heating the used catalysts, and the amount of the desorbed NO$_2$ is larger than that integrated the concentration of NO$_2$ in the feed gas. The results indicate that the oxidation of NO with oxygen over Co-Phc/YZ and Co-Phc/Al$_2$O$_3$ proceeds at 30 °C. The Co-Phc/YZ and Co-Phc/Al$_2$O$_3$ catalyst were regenerated by water washing and could be used again for the removal. The ESR spectra for Co-Phc/YZ and Co-Phc/Al$_2$O$_3$ revealed the hyperfine structure of β-form cobalt phthalocyanine. The hyperfine coupling constant is determined to be $A = 0.0093$ cm^{-1} for Co-Phc/YZ, and $A = 0.0097$ and $B = 0.033$ cm^{-1} for Co-Phc/Al$_2$O$_3$. The load of β-form cobalt phthalocyanine on alumina show little change of $g_\parallel$ and $g_\perp$ value, but hyperfine

coupling constants of A and B change significantly. Similarly, the load of β-form cobalt phthalocyanine on acidic Y-type faujasite also shows little change of $g_\parallel$ value, but the hyperfine constant of A also changes remarkably, as like β-form cobalt phthalocyanine in sulfuric acid solution. The result suggests that the A values perhaps depend on the acidity of proton form Y-type faujasite and alumina. The superhyperfine structure appears on admittance of NO (0.2 Pa) and O$_2$ (10 Pa). The superhyperfine constants are determined to be 0.0015 cm^{-1} for Co-Phc/YZ and 0.0016 cm^{-1} for Co-Phc/Al$_2$O$_3$. The superhyperfine lines support the formation of Co–N bond between NO$_x$ and cobalt of phthalocyanate. Therefore, it is concluded that the formation of Co–NO$_x$ bonding and large adsorption capacities of NO$_x$ are effective for the NO$_x$ removal over the catalysts.

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