Original Communication

J. Jpn. Soc. Colour Mater. (SHIKIZAI), 63 (7), 385-391, 1990

Studies on Phthalocyanine Type Compounds (Part V*)

Catalytic Behavior of Metal Phthalocyanine in the Hydrogen Atmosphere

Keiichi SAKAMOTO**, Jun SONOBE** and Fukumatsu SHIBAMIYA**

Abstract

Metal phthalocyanine (M-PC) type compounds as functional substances have attracted major interest. However, M-PCs have been seldom used for industrial catalysts. The purpose in this study is to develop a new industrial catalyst using M-PCs and to elucidate the mechanism of the catalytic effect. We have found that Co-PC has a more excellent effect on dehydrogenation of tetralin and hydrocracking of heavy oil in comparison to conventional catalysts. M-PCs can hold some hydrogen atoms through the reduction in the PCs themselves. Further, hydrogen atoms are held on the propagating plane of M-PCs and/or absorbed into the crystal lattice. Therefore, M-PCs can hold a large amount of hydrogen and show a high catalytic effect. The ligand is much concerned with the hydrogen carrier since M-PCs' catalyses are affected by the number of electrons on $3d^4s^2$ orbital in the metal and the molecular orbital of the ligand.

Key-words : *Phthalocyanine, Hydrogen treatment, Polymorphism, XPS, Catalytic effect*

1. Introduction

Metal phthalocyanine (M-PC) type compounds, such as Cu-PC, Ni-PC and so on, are known as blue to green metal organic complexes which have been used as dyestuffs and pigments.

Recently M-PCs have attracted major interest as functional substances : that is, they have been used for photoconductors¹⁾, semiconductors²⁾ or catalysts^{3)~8)} since they consist of a porphyrine structure similar to that of porphyrin with π electrons along the conjugated path.

It is especially expected that M-PCs may act as

a gas carrier similar to a hemoglobin and accelerate decomposition of H_2O_2 similar to enzymolysis.

M-PCs and their derivatives can be employed as catalysts for various reactions, such as oxidation³⁾, dehydrogenation⁴⁾, desulfurization⁵⁾, decomposition⁶⁾ and carbonization⁷⁾, if the central metal atom in the macrocycle is appropriately exchanged with another one. Actually, it has been reported that M-PCs and their derivatives are more effective catalysts than the conventional ones applied to the above-mentioned reactions.

In spite of having more effective catalysis, M-PCs have been utilized only in a few fields as catalysts^{9),10)}, and few fundamental experiments have been performed to develop M-PCs as industrial catalysts.

Therefore, we have once reported on the basis of the kinetics of reaction that M-PCs as the catalyst of the hydrogen-donor-hydrocarbon exhibited a higher effect than silica-alumina for dehydrogenation which involves with the hydrogen-transfer reaction from the hydrogen-donor-hydrocarbon such as tetralin¹¹⁾, and further have found that the Co-PC used for hydrocracking catalyst accelerated the decomposition and inhibited the formation

Received May 14, 1990

* The preceding papers, A) K. Sakamoto, J. Sonobe, F. Shimizu and F. Shibamiya, J. Chem. Soc. Jpn. (Nippon Kagaku Kaishi), 1989, 1111, B) K. Sakamoto and F. Shibamiya, Dyestuffs Chem. (Sen-ryou to Yakuhin) 33, 312 (1988) and C) K. Sakamoto and F. Shibamiya, J. Jpn. Soc. Colour Mater. (Shikizai), 59, 517 (1986)

** College of Industrial Technology, Nihon University 1-2-1 Izumi-cho, Narashino-shi, Chiba 275, Japan

Metal phthalocyanine (M-PC)

Cobalt tetrapyrrolineporphyrizine (Co-TPP)

Fig. 1. Molecular structure of metal phthalocyanine and Cobalt tetrapyrrolineporphyrizine

of coke as by-products¹²⁾. Then, in this study the reduction in the M-PCs in the hydrogen atmosphere is discussed on the basis of the dislocation of M-PCs' crystal lattices.

2. Experimental

2.1 Preparation of M-PCs

The PC-type compounds used in this study were Fe-PC, Co-PC, Ni-PC, Cu-PC and cobalt tetrapyrrolineporphyrizine (Co-TPP). The constitutional formulas of the M-PC and the Co-TPP are shown in **Figure 1**.

The M-PC compounds were synthesized in accordance with Wyler's method^{11)~14)} using phthalic anhydride.

Co-TPP was obtained from 2,3-pyridine dicarboxylic acid, urea, respective metal salts, ammonium molybdate as a catalyst, and 1,2,4-trichlorobenzene as a solvent.

2.2 Experimental procedure

2.2.1 Thermal treatment of M-PCs

M-PCs were thermally treated in an autoclave. The reactor was charged with 3g of a PC type compound, followed by evacuation and flashing with nitrogen to eliminate oxygen from the system. The leakage of the system was then checked under pressure of 100 kg/cm² with nitrogen for 12 hours. After evacuated and flashed with hydrogen, the reactor was pressurized to 50 kg/cm² and the leakage was checked by the method using a soap solution. We set up the time when the reactor was heated up to 380°C at the rate of 3°C/

minute as the starting treatment time. In dehydrogenation of tetralin¹¹⁾ and hydrocracking of heavy oil¹²⁾, the reactor was charged with 10 g of each sample and 0.1 g of the catalyst and was pressurized to 10 kg/cm² with hydrogen.

2.2.2 Spectroscopy

Ultraviolet-visible spectra were recorded on a Shimadzu UV-2100, ultraviolet-visible spectrophotometer. Each sample was prepared to be 0.025 mg/ml in pyridine or saturated solution in 1-chloronaphthalene.

2.2.3 X-ray analysis

X-ray diffraction patterns were obtained using a Rigaku-denki X-ray diffractometer RAD-B. Cu K α radiation was used to obtain the X-ray scan.

XPS spectra were recorded on a Shimadzu ESCA-750 spectrometer equipped with a data-processor ESPAC-1000. Binding energies were corrected by taking C 1s=284.6 eV.

3. Results and Discussion

Table 1 shows the first-order constant for dehydrogenation of tetralin¹¹⁾ using various kinds of catalysts. The catalytic effect of M-PCs on dehydrogenation decreased in the order of Co, Ni and Cu. This is considered to be ascribed to the electron configuration of the central metals in the PC molecules.

Figure 2 shows the yield of hydrocracking of heavy oil¹²⁾ at 180 minutes. The liquid products obtained from distillation are fractionated having a range of boiling point below 280°C. The distilled

Table 1. First-order constant of dehydrogenation of tetralin

Temperature (°C)	No catalyst	Co-PC	Co-TPP	Ni-PC	Cu-PC
300	6.69×10^{-6}	3.95×10^{-5}			
350	1.14×10^{-5}	9.93×10^{-5}	1.66×10^{-4}		
380	1.08×10^{-4}	5.19×10^{-4}	2.31×10^{-4}	3.74×10^{-4}	2.25×10^{-4}

Fig. 2. Yield of hydrocracking of heavy oil obtained at 180 minutes

Fig. 3. Relationship between thermal treatment time and hydrogen pressure

residue was also fractionated into BS-HS, BS-HI and BI, where B, H, S and I means benzene, n-heptane, soluble and insoluble, respectively. The liquid products and BS-HS are commonly called liquefied oils. In the previous paper¹²⁾, BI was also separated into BI-TS and BI-TI (T means tetrahydrofuran).

The Co-PC catalyst used here inhibits the formation of by-products such as BI-TS and BI-TI, and therefore promotes hydrocracking more effectively than commercial ones used industrially. The

results of structural analysis¹⁵⁾ show that the hydrocracking products are considered to have the most decomposed molecular structure of three method used here¹²⁾.

Figure 3 shows the change in hydrogen consumption viewed from the pressure decrease in the autoclave with treatment time when Co-, Fe- and Ni-PCs were used. The hydrogen consumption increased in the following order; Ni-PC, Fe-PC and Co-PC. The hydrogen pressure was almost constant after around 180 minutes. The rate of

the decrease in hydrogen pressure till constant value in M-PCs could be estimated to be between 0.02 and 0.05 kg/cm²·min, while the Co-TPP system hardly showed any change of hydrogen pressure during the thermal treatment.

It is considered that the observed pressure-decrease comes from the reduction in and absorption into M-PCs by hydrogen. The reduction in M-PCs can take place at the central metal atom and/or 16 peripheral carbon atoms of the four phenylene rings¹⁶⁾, and it is known that hydrogen bonding to 4 nitrogen atoms occurs on the porphyrine ring¹⁷⁻¹⁹⁾. In addition, the transient reduction in Co-PC¹⁶⁾ involves hydrogenation at the α and β carbon atoms of the pyrrole rings in the molecule.

On the other hand, it is difficult to reduce the Co-TPP, since the nitrogen atoms in the pyridine rings only coordinate hydrogen atoms due to quaternarization.

Figure 4 shows visible spectra of the Co-PC before and after thermal treatments in pyridine. The maximum absorbance in the Co-PC appeared at 648 nm before the thermal treatment and shifted by about 10 nm to the longer wavelength after the thermal treatment. It is considered that the shifted maximum absorbance is due to the bathochromic effect coming from the reduction in the Co-PC.

Fig. 4. Visible spectra of Co-PCs obtained in pyridine
(A): After thermal treatment
(B): Before use

The reduced Co-PC can hold a large amount of hydrogen through the cross-linking by phenylene rings and nitrogen atoms at the peripheral site in the porphyrine as mentioned above. The reduction in M-PC like the reduced Co-PC which is produced in the thermal treatment is very susceptible to oxidation by air^{20), 21)}.

Bansho et al. reported two types of the reduced Co-PC to exhibit a green showing the bathochromic effect and a reddish violet the hypsochromic²¹⁾. In addition, they also reported various types of reduced form in metal-free PC²⁰⁾.

When treated thermally, Co-PC, Ni-PC and Cu-PC powders became darker than before, while Fe-PC powder became fused. The unusual behavior appearing for Fe-PC may be due to the chlorine atoms from the ferric chloride used in the synthesis.

Fig. 5. Ultraviolet-visible spectra of Co-PCs and Ni-PCs in 1-chloronaphthalene
A: Co-PC, before use
B: Co-PC, 60 minutes
C: Co-PC, 120 minutes
D: Co-PC, 180 minutes
E: Co-PC, 480 minutes
F: Ni-PC, before use
G: Ni-PC, 480 minutes

Figure 5 shows ultraviolet-visible spectra of the Co-PC and Ni-PC measured in 1-chloronaphthalene as a solvent, with small shifts of the maximum absorbance by about 1 nm. However, the spectral distributions on the whole differ from the ones before the thermal treatment and also the peak at 740 nm in Ni-PC disappears after the thermal treatment. It has been found in Co-PC that the maximum absorbance shifted independently of the thermal treatment time. It is clear that the change of spectral distribution mainly shows a hyperchromic effect ascribed to the transformation in the M-PCs reduced by hydrogen. Allowed to stand for some time after the thermal treatment, the spectra changed into the same as before, since the reduced types of M-PCs were rapidly oxidized by air as Bansho²¹⁾ reported.

X-ray diffraction patterns before and after thermal treatments are shown in **Figure 6**.

Fig. 6. X-ray diffraction patterns of M-PCs

- a : Co-PC, before use
- b : Co-PC, 60 minutes
- c : Co-PC, 120 minutes
- d : Co-PC, 480 minutes
- e : Ni-PC, before use
- f : Ni-PC, 480 minutes
- g : Fe-PC, before use

X-ray diffraction patterns of the stable β crystal form show the maximum intensity at 9° with the next strongest lines at 7° and 18°, while the metastable α crystal form has the maximum intensity at 7° with the next strongest line at 14°.

Before the thermal treatment the M-PCs were the stable β crystal forms with two strong lines at 7° and 9°. On the other hand, it was observed that the M-PCs underwent some dislocation after the thermal treatment; for instance, the Co-PC was transformed to the metastable α crystal form after the thermal treatment for 480 minutes.

The dislocation observed in Co-PC occurred gradually with the increase in the thermal treatment time: the stable β crystal form was observed at 0 and 60 minutes and the X-ray diffraction pattern showed the presence of an intermediate between α and β at 120 minutes.

The phenomena similar to the case of the Co-PC could be observed in other M-PCs, for instance, the crystal of Ni-PC showed an intermediate between stable β and metastable α even at 480 minutes.

However, though the untreated Fe-PC took a stable β crystal form, no X-ray diffraction patterns for thermally treated one could be obtained because of its fusion during the treatment as described before.

The stable β crystal form is a needle crystal having a monoclinic system^{22)~25)}. The β Ni-PC has the crystal structure inclined by approximately 45.8° to the b axis of propagating planes stacked in parallel with 4.79 Å spacing. Other M-PCs have similar crystal structures except Pt-PC²⁵⁾.

In the β crystal form, the propagation plane (010) exposes the molecular plane to reactant molecules²⁶⁾, since the central metal in the outer-most porphyrine ring is sited on one of the nitrogen atoms cross-linked between pyrrole molecules in the lower ring. A reactant can encounter the molecular plane, the (010) plane, of the M-PC. Other reactants can come into contact with sides of the stacked porphyrine rings²⁶⁾ and so some reactants can be absorbed into the lattice if they are small enough to enter the space between the two rings.

From the just-described, the M-PC can be regarded as a molecule with 16 carbon and 4 nitrogen atoms at the peripheral site and/or the central metal to be reduced, or as a crystal to absorb hydrogen atoms into the lattice. Consequently, the M-PC can have a large amount of hydrogen and so show an excellent catalytic effect.

The metastable α crystal form obtained after the thermal treatment shows a tetragonal system²⁷⁾.

Table 2. Binding energies of N 1s and Co 2p_{3/2} in XPS spectra of Co-PC before and after thermal treatment

	Before use	After thermal treatment			
		Time of thermal treatment (min.)			
		0	60	120	480
N 1s	398.8	400.2	400.1	400.4	401.7
Co 2p _{3/2}	781.0	781.6	781.0	781.0	781.6

The α M-PC differs from the $\beta^{29)}$ in the stacked structure of the molecular plane, that is, the central metal is situated not on nitrogen atoms in the peripheral but on a half distance of the metal to the nitrogen in the lower porphyrine ring^{29),30)}. It is inferred from this reason that the α crystal form can have a less absorptive capacity to hydrogen as compared with the β . Accordingly, the central metal atoms in M-PCs have a great influence on both the catalytic behavior coming from the electron configuration^{11),31)} and the rate of dislocation by heating. Therefore, the Ni-PC takes a long time for the crystal to dislocate, since hydrogen atoms are more slowly absorbed into the lattice of the Ni-PC than that of the Co-PC.

Table 2 shows binding energies of N 1s and Co 2p_{3/2} in XPS spectra of Co-PC before and after thermal treatments.

Binding energies of Co 2p_{3/2} appeared independent of the length of the thermal treatment time and remained constant at 781.0 eV. The peak of N 1s shifted to higher binding energies with the thermal treatment time and the maximum distance between the peaks before and after thermal treatments was 2.9 eV. The peak of C 1s appeared symmetrically before the thermal treatment but asymmetrically after that. Similar phenomena were also observed in other M-PCs.

It is considered that some reactions occurred on the atoms of nitrogen and carbon contained in the ligand.

These results are in agreement with the report that N 1s peak appeared at 398.6 eV and, after the contact of Fe-PC with formic acid, at higher binding energy, 400.1 eV¹⁸⁾.

We can say that the π electrons of the ligand contribute to the catalysis of M-PCs. The difference in the catalysis of M-PCs comes from the fact that the electron configuration of the central metals of Fe, Co and Ni can be given by 3d¹⁰4s² (n equals to 6, 7 and 8, respectively), and Cu 3d¹⁰4s¹. A metal in the phthalocyanine macrocycle forms dsp₂ metal hybrid receptor orbital³¹⁾,

resulting in the change in electron density of the ligand.

References

- 1) P. J. Regensburger : *Photochem. Photobiol.*, **8**, 429 (1968)
- 2) K. F. Schoch, Jr., B. R. Kundalder and T. J. Maeks : *J. Am. Chem. Soc.*, **101**, 7071 (1979)
- 3) N. Takamiya, T. Yamaguchi, T. Iwatsuki and S. Murai : *J. Chem. Soc. Jpn.*, **1977**, 1775
- 4) N. Takamiya, M. Takano, N. Miyata and H. Shouji : *ibid.*, **1981**, 326
- 5) N. Takamiya, T. Iwatsuki, T. Nagai and S. Murai : *ibid.*, **1979**, 825
- 6) J. Manassen and S. Khalif : *J. Am. Chem. Soc.*, **88**, 1943 (1966)
- 7) Y. Ohkatsu, K. Nakazawa and T. Osa : *J. Jpn. Petroleum Institute*, **22**, 388 (1979)
- 8) O. Hirabaru, T. Nakase, K. Hanabusa, H. Shirai, K. Takemoto and N. Hojo : *J. Chem. Soc. Dalton Trans.*, **1984**, 1485
- 9) U. P. S., 2853432 (1958), U. P. S., 2882224 (1959), U. S. P., 2921020 (1960)
- 10) H. Shirai : *Sen-i Gakkaishi*, **41**, 267 (1985)
- 11) K. Sakamoto and F. Shibamiya : *Dyestuffs Chem.*, **33**, 312 (1988)
- 12) K. Sakamoto, J. Sonobe, F. Shimizu and F. Shibamiya : *J. Chem. Soc. Jpn.*, **1988**, 1111
- 13) K. Sakamoto, M. Yoshioka and F. Shibamiya : *J. Jpn. Soc. Colour Mater.*, **58**, 121 (1985)
- 14) K. Sakamoto and F. Shibamiya : *ibid.*, **59**, 517 (1986)
- 15) J. G. Speight : *Fuel*, **49**, 134 (1970)
- 16) F. H. Moser and A. L. Thomas : "The Phthalocyanine Compounds" p. 59, Reinhold Publishing Corporation (1963)
- 17) S. Tanaka, T. Onishi and K. Tamaru : *Bull. Chem. Soc. Jpn.*, **41**, 2557 (1968)
- 18) T. Kawai, M. Soma, Y. Matsumoto, T. Onishi and K. Tamaru : *Chem. Phys. Lett.*, **37**, 378 (1976)
- 19) A. N. Sidorov : *Spektroskopiya*, **13**, 668 (1962)
- 20) Y. Banshou, T. Shimura and A. Fukazawa : *J. Chem. Soc. Jpn.*, **1972**, 1485
- 21) Y. Banshou, T. Shimura, O. Uyeda, H. Tanzaki and K. Takei : *Kogyo Kagaku Zasshi*, **74**, 1870 (1974)
- 22) J. M. Robertson : *J. Chem. Soc.*, **1936**, 1195
- 23) J. M. Robertson : *ibid.*, **1936**, 1736
- 24) J. M. Robertson and I. Woodward : *ibid.*, **1937**, 216
- 25) J. M. Robertson and I. Woodward : *ibid.*, **1940**, 1195

- 26) Y. Suda : *Dyestuffs Chem.*, **27**, 171 (1982) *Chem.*, **12**, 41 (1967)
27) M. Ashida, N. Uyeda and E. Suito : *Bull. Chem. Soc. Jpn*, **39**, 2616 (1966) 30) I. Kumano : *Den-shi Shashin Gakkaishi*, **22**, 111 (1984)
28) B. Honigmann and H. Lenne : *Z. Krist.*, **122**, 185 (1965) 31) H. S. Nalwa : *J. Electr. Mater.*, **17**, 291 (1988)
29) E. Suito, N. Uyeda and M. Ashida : *Dyestuffs*
-