

Origins of Remarkable Catalytic Activity of Cobalt Tetraphenylporphyrin Supported on Some Titanias

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Catalytic activities of CoTPP (cobalt tetraphenylporphyrin) supported on two kinds of titania, TiO₂-120s and TiO₂-300, against CO-O₂, NO-CO, and NO-H₂ reactions were found to depend remarkably on the titania and the conditions of preheat treatment in vacuo. CoTPP/TiO₂-120s-250 (pretreated at 250 °C) exhibited larger activities for the former two reactions than CoTPP/TiO₂-300-200 (pretreated at 200 °C), whereas the latter catalyst exhibited a larger one for the last reaction. Detailed studies on reaction kinetics, single and competitive adsorption, catalyst poisons, electron spin resonance, thermogravimetry during the pretreatment, and the solubility of the supported complex were performed in order to reveal origins of such catalytic performances of CoTPP complex on the titania surface. It is suggested that oxidative oligomerization of CoTPP into dimeric or trimeric forms and oxygen vacancy on the reducible titania surface were induced by the pretreatment in the former catalyst to provide remarkable activation abilities against CO, NO, and O₂. In contrast, the original structure of CoTPP is concluded more suitable for the formation of an anion radical in the ligand through the electron donation from the properly dehydrated surface of rather stable titania to exhibit better ability for H₂.

Introduction

We have reported that CoTPP (cobalt tetraphenylporphyrin) supported on titania prepared from titanil sulfate showed remarkable catalytic activities for the NO reduction with H₂ and CO, and CO oxidation with oxygen.¹⁻⁶ For example, its activity for the oxidation of CO was significant at -72 °C and was much superior to that of commercial hopcalites.⁵ Previous studies^{5,6} suggest catalytic performances of CoTPP on TiO₂ strongly owing to the preparation conditions (drying or calcination temperatures of titania and preheat treatment conditions after supporting) of the catalysts. There will be an interesting chemistry in terms of the interaction between the coordination complex and titania support to exhibit remarkable catalytic activities since structures of both substances were found to be altered considerably under the preparative conditions.^{3,5,6}

CoTPP supported on TiO₂, which was prepared from titanil sulfate and calcined at 300 °C (TiO₂-300), was found to form its anion radical (Co^{(2-δ)+}TPP⁻) due to the electron transfer from TiO₂ by the evacuation at 200 °C.³ This anion radical species was estimated to be the catalytic active species regardless of preparative conditions.^{3,5,6} However, there still remain unsolved questions about the structural differences in the active species and interactive sites of TiO₂ due to the preparative conditions to exhibit contrast catalytic performances.

Thus, in the present study, the catalytic activities, kinetics, adsorption abilities, poisons, and structures of the complex and titania surface were compared to discuss

the origin of their catalytic activities, comparing three representative catalysts, CoTPP/TiO₂-120s-250, CoTPP/TiO₂-120s-200, and CoTPP/TiO₂-300-200. Since two kinds of starting titanias and two heat treatment conditions brought about marked differences in their catalytic performances, such studies are expected to provide some keys to reveal the origins of their catalytic activities.

Experimental Section

Cobalt tetraphenylporphyrin (CoTPP) was synthesized by Adler's method.⁷ TiO₂-300 and TiO₂-120s, which were prepared by precipitation from titanil sulfate without and with seeds and calcined at 300 °C (Brunauer-Emmett-Teller (BET) surface area 170 m²/g, 8.3 wt % SO₄) and 120 °C (240 m²/g, 8.1 wt % SO₄), respectively, were both provided by Titan Kogyo Co. CoTPP was impregnated onto titania using a benzene solution to give a concentration of 5 wt %.

CoTPP/TiO₂-300 and CoTPP/TiO₂-120s, thus prepared, were evacuated (2 × 10⁻³ Torr) at 200 °C 1 h or 250 °C 2 h before the reaction to give three kinds of catalysts: CoTPP/TiO₂-300-200, CoTPP/TiO₂-120s-200, and CoTPP/TiO₂-120s-250.

The catalytic oxidation of CO with O₂ was carried out at 0 °C, using a circulation reactor (volume 800 mL, circulation rate 500 mL/min). The catalyst (0.2 g) was diluted with SiC (1.0 g) in the catalyst bed to release the heat of reaction. Partial pressures of CO and O₂ were 50 and 100 Torr, respectively.

The reduction of NO with CO or H₂ was carried out at 100 °C by using the same reactor. The catalyst (4 g) was piled in the catalyst bed to pass gases through it. Partial pressures of NO, CO, and H₂ were 100, 200, and 200 Torr, respectively. The gases were analyzed by a gas chromatograph.

Adsorption measurements were done volumetrically using 1 g of catalyst under variable pressures of 1-500 Torr at 0 °C. Competitive adsorption of NO and CO was measured at 70 °C. Electron spin resonance (ESR) measurements of the catalysts were performed at room temperature in vacuo or reactant gases.

Solubilities of the complex of CoTPP/TiO₂-120s-250 were examined by Soxhlet extraction using benzene, pyridine, and quinoline as a solvent. The pyridine-soluble fraction was further fractionated by column chromatography (silica gel C-200, Wako Junyaku Co.; tetrahydrofuran as an eluting solvent). The fractionated materials were analyzed by visible and IR spectroscopies and molecular weight measurement (vapor pressure osmometer) in addition to microanalyses.

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Table I. Effects of the Support on the Catalytic Activity of CoTPP/TiO₂

support-HTT ^f	reaction rate ^a (m, n) ^b		
	CO-O ₂ ^c	NO-CO ^d	NO-H ₂ ^e
TiO ₂ -120s-250	1.5 (1, 0)	2.2 (0.65, 0.61)	5.8×10^{-2} (-0.5, 1.3)
TiO ₂ -120s-200	6.8×10^{-1}	1.3	8.7×10^{-2} (-0.5, 0.6)
TiO ₂ -300-200	3.0×10^{-1} (0, 1)	6.5×10^{-1} (0, 0.9)	1.0×10^{-1} (-0.9, 0.6)

^a (mol/mol of CoTPP)/min. ^b The numbers in parentheses are reaction orders: CO^mO₂ⁿ, NO^mCOⁿ, NO^mH₂ⁿ. ^c [CO]/[O₂] = 50/100 (Torr), catalyst 0.2 g, at 0 °C. ^d [NO]/[CO] = 100/200 (Torr), catalyst 4 g, at 100 °C. ^e [NO]/[H₂] = 100/200 (Torr), catalyst 4 g, at 100 °C. ^f Heat treatment temperature (°C).

Table II. Catalytic Activities of CoTPP/TiO₂-120s-250 and CoTPP/TiO₂-300-200 in the Repeated Reactions

	reaction rates, (mol/mol of CoTPP)/min ^a			
	CoTPP/TiO ₂ -120s-250		CoTPP/TiO ₂ -300-200	
	first	second ^b	first	second ^b
CO-O ₂ ^c	1.5	5.8×10^{-1}	3.0×10^{-1}	3.1×10^{-2}
NO-H ₂ ^d	5.8×10^{-2}	4.6×10^{-2}	1.0×10^{-1}	7.3×10^{-2}
NO-CO ^e	2.2	2.2	6.5×10^{-1}	6.5×10^{-1}

^a Initial rates. ^b Second run after 3-h reaction of the first run followed by evacuation at the reaction temperature for 1 h. ^c [CO]/[O₂] = 50/100 (Torr), catalyst 0.2 g, at 0 °C. ^d [NO]/[H₂] = 100/200 (Torr), catalyst 4 g, at 100 °C. ^e [NO]/[CO] = 100/200 (Torr), catalyst 4 g, at 100 °C.

Results

Catalytic Activities of CoTPP-Supported Titanias.

The catalytic activities (initial rates) of CoTPP/TiO₂'s for CO-O₂ (CO + 1/2 O₂ → CO₂), NO-CO (2NO + CO → N₂O + CO₂, N₂O + CO → N₂ + CO₂), and NO-H₂ (NO + H₂ → 1/2 N₂ + H₂O) reactions are summarized in Table I. Although the rates of the reactions decreased always in the order CO-O₂, NO-CO, and NO-H₂ regardless of the catalysts, activity orders of catalysts varied from one reaction to another. CoTPP/TiO₂-120s-250 exhibited the highest activity in the CO-O₂ and NO-CO reactions which was 15 and 3.5 times larger than those of CoTPP/TiO₂-300-200, respectively. In contrast, the latter catalyst exhibited 2 times higher activity in the NO-H₂ reaction than CoTPP/TiO₂-120s-250. CoTPP/TiO₂-120s-200 showed the intermediate activities for all reactions.

The reaction orders in the substrates are also included in Table I. Some contrast features were observable with CoTPP/TiO₂-120s-250 and CoTPP/TiO₂-300-200. In the CO-O₂ reaction, the orders in CO were first and zero on CoTPP/TiO₂-120s-250 and CoTPP/TiO₂-300-200, respectively. The orders in O₂ were just reverse. In the NO-CO reaction, CoTPP/TiO₂-120s-250 exhibited similar values of orders (around 0.6) in both NO and CO, whereas CoTPP/TiO₂-300-200 exhibited 0 and 0.9, respectively. Although the orders in H₂ of the NO-H₂ reaction were higher than those in NO on both catalysts, the values of both orders on CoTPP/TiO₂-120s-250 were much larger than those on CoTPP/TiO₂-300-200. Retardation by NO was more marked on the latter catalyst. The reaction orders on CoTPP/TiO₂-120s-200 appeared again intermediate to those of the former two catalysts. Thus, the reaction orders were very variable on the catalysts, indicating variable extents of interaction between the substrates and their active sites.

The catalytic activities of CoTPP/TiO₂-120s-250 and CoTPP/TiO₂-300-200 in the second runs are summarized in Table II, where the catalysts were evacuated for 1 h at the reaction temperature before the second run after the first run. Except for the NO-CO reaction, a considerable

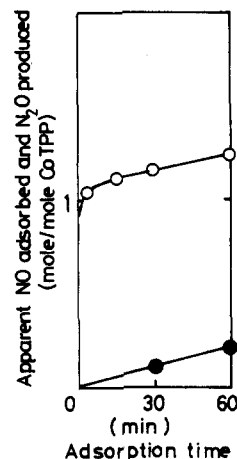


Figure 1. Time course of NO adsorption on CoTPP/TiO₂-300-200 at 70 °C $P_{\text{NO}}(\text{init}) = 100$ Torr: O, adsorbed NO estimated from pressure decrease; ●, N₂O produced (NO base).

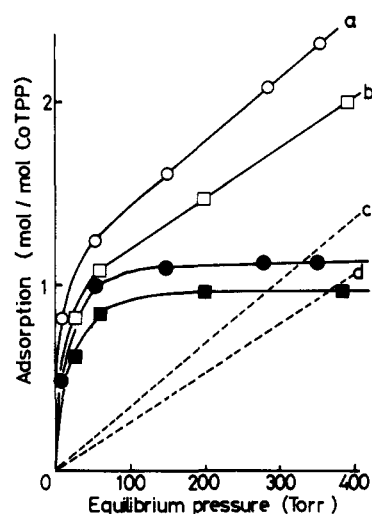
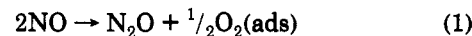


Figure 2. Adsorption isotherm of NO on CoTPP/TiO₂-120s-250 and CoTPP/TiO₂-300-200 at 70 °C: a, CoTPP/TiO₂-120s-250; b, CoTPP/TiO₂-300-200; c, physisorption on CoTPP/TiO₂-120s-250; d, physisorption on CoTPP/TiO₂-300-200; e, chemisorption on CoTPP/TiO₂-120s-250; f, chemisorption on CoTPP/TiO₂-300-200.

decrease of catalytic activity in the second run was observable on both catalysts. The decrease in the CO-O₂ reaction was most marked. Poisons are described in a later section. The activities of the catalysts in any reaction, however, were restored to the initial ones by the evacuation for 2 h at 250 or 200 °C, respectively, according to the preparation procedures.

Adsorption Abilities of CoTPP on Titanias. Figure 1 shows the adsorption profile of NO on CoTPP/TiO₂-300-200 at 70 °C. After very quick adsorption of NO within 5 min, the amount of apparent adsorption increased slowly and linearly with the time due to decomposition to N₂O (eq 1). Hence, the amount of real adsorption under a



certain equilibrium pressure was obtained as the value of intercept at zero adsorption time by extrapolating the linear part of the adsorption increase in Figure 1.

The isotherms of NO adsorption at 70 °C thus measured on CoTPP/TiO₂-120s-250 (line a) and CoTPP/TiO₂-300-200 (line b) by using fresh catalysts for every point are illustrated in Figure 2. Linear parts of the isotherms at higher pressures may correspond to physisorption of NO

Table III. Adsorption Abilities of CoTPP Supported on TiO₂-120s and TiO₂-300

catalyst	adsorption amounts, molecules/CoTPP					
	NO ^{a,e}	O ₂ ^{a,b,f}	O ₂ ^{a,c,f}	CO ^{a,f}	H ₂ ^{d,f}	
CoTPP/TiO ₂ -120s-250	1.1	0.5	0.2	2.4	0.5	0.1
CoTPP/TiO ₂ -120s-200		0.3	0.2	2.4		0.2
CoTPP/TiO ₂ -300-200	1.0	0.8	0.8	1.4	0.2	0.3

^a Equilibrium pressure 100 Torr. ^b First run. ^c Second run after evacuation at 0 °C. ^d Initial pressure 500 Torr. ^e Adsorption temperature 70 °C. ^f Adsorption temperature 0 °C.

on TiO₂. Since the physisorption must be null at zero pressure, lines c and d, which are parallel to the linear parts of lines a and b, respectively, are assumed to describe the profiles of physisorption on TiO₂. In fact, almost the same adsorption profiles were reproduced on TiO₂'s after the evacuation at the preparation conditions. Therefore, the isotherms of chemisorption (lines e and f) on supported CoTPP were obtained by subtracting lines c and d from lines a and b, respectively. They were saturated at about 100 Torr of NO to give similar NO/CoTPP ratios of 1.1 and 1.0, respectively, on CoTPP/TiO₂-120s-250 and CoTPP/TiO₂-300-200 as shown in Table III.

Adsorption abilities of three catalysts against O₂ were measured at 0 °C to obtain isotherms. The adsorbed amounts in the second run after the evacuation at 0 °C decreased in comparison with those in the first run on CoTPP/TiO₂-120s-250 and -200, suggesting some extent of its irreversible adsorption. However, evacuation at 250 and 200 °C after the second run restored the adsorption abilities of CoTPP/TiO₂-120s-250 and CoTPP/TiO₂-120s-200, respectively. In contrast, O₂ adsorbed reversibly on CoTPP/TiO₂-300-200. Because adsorptions on all catalysts were saturated at about 100 Torr, the adsorption amounts in the first and second runs at 100 Torr are summarized in Table III. Whole adsorption ability against O₂ decreased in the order CoTPP/TiO₂-300-200 > CoTPP/TiO₂-120s-250 > CoTPP/TiO₂-120s-200; however, CoTPP/TiO₂-120s-250 exhibited much larger irreversible adsorption, the difference between the first and second adsorption, than CoTPP/TiO₂-120s-200.

In contrast to O₂, CO and H₂ adsorbed on all catalysts reversibly at 0 °C. Adsorption abilities for CO were obtained from isotherms at 100 Torr of equilibrium pressure by subtracting its physisorption at the same pressure, whereas those against H₂ were measured under a fixed initial pressure of 500 Torr, because the adsorption was very small at low pressures. The ratios of adsorbed molecules to CoTPP molecules are summarized in Table III. The adsorption ability for CO decreased in the order CoTPP/TiO₂-120s-250, CoTPP/TiO₂-120s-200, and CoTPP/TiO₂-300-200, whereas that for H₂ decreased in the reverse order, although the adsorbed amounts of these substrates were much different. TiO₂-120s and TiO₂-300 evacuated at 200 and 250 °C, respectively, for 1 h exhibited only physisorption abilities for CO under the present conditions. The ratios of adsorbed CO to CoTPP molecule exceeded unity on all catalysts as shown in Table III, indicating a significant contribution of two-molecule adsorption on the two axial coordination sites of the Co ion of CoTPP. The ratios decreased to less than unity at 70 °C, where CoTPP/TiO₂-120s-250 adsorbed much more than CoTPP/TiO₂-300-200, suggesting its strong ability.

Competitive adsorption of CO and NO was measured over CoTPP/TiO₂-120s-250 and CoTPP/TiO₂-300-200 at 70 °C. The time course of the composition change in the gas phase on CoTPP/TiO₂-120s-250 is illustrated in Figure 3, where the mixture of CO and NO (100/100 Torr) was

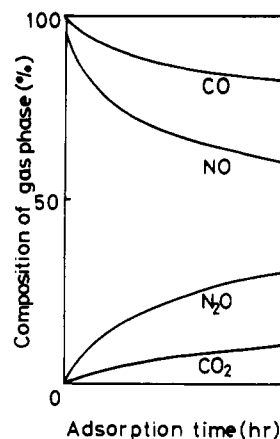


Figure 3. Time course of the composition in the gas phase in competitive adsorption of NO and CO on CoTPP/TiO₂-120s-250 at 70 °C (catalyst 4 g) $P_{\text{NO}} = P_{\text{CO}} = 100$ Torr was introduced.

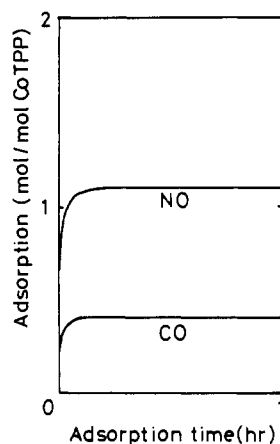
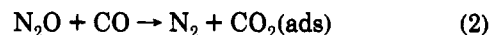
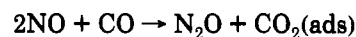


Figure 4. Adsorption of NO and CO in their competitive adsorption on CoTPP/TiO₂-120s-250 at 70 °C: equilibrium pressure, NO 72.7 Torr, CO 51.6 Torr; other conditions, see Figure 3.

introduced. Since the reaction between NO and CO (eq 2) to produce N₂O, N₂, and CO₂ took place simultaneously



at this temperature, adsorption amounts of NO and CO corrected by subtracting the amounts consumed by the reaction are illustrated in Figure 4, where the extent of reaction was measured by analyzing produced N₂O and N₂ since a considerable amount of CO₂ adsorbed on the support.³ CO consumption was assumed to be equal to the sum of N₂O and N₂ produced because equimolar CO₂ was confirmed by the evacuation after the reaction. As shown in Figure 4, both substrates adsorbed very quickly and leveled off after 10 min. From Figure 4, the chemisorption amounts of each substrate were obtained by subtracting the amount of physisorption estimated from each isotherm at 70 °C, where equilibrium pressures of NO and CO were 51.6 and 72.7 Torr, respectively. The ratios of adsorbed molecules to a CoTPP molecule thus obtained over two catalysts are summarized in Table IV and compared with the values in their single adsorption. The ratios of 0.9 mol of NO/mol of CoTPP and 0.2 mol of CO/mol of CoTPP, respectively, were obtained on CoTPP/TiO₂-120s-250. These values were slightly less than the amounts of their respective single adsorption.

Table IV. Competitive Adsorption of NO and CO on CoTPP/TiO₂-120s-250 and CoTPP/TiO₂-300-200 at 70 °C^a

	chemisorption amounts, molecules/CoTPP	
	CoTPP/TiO ₂ -120s-250	CoTPP/TiO ₂ -300-200
single ads	1.0 ^b	0.9 ^d
NO		
competitive ads	0.9 ^b	0.9 ^d
single ads	0.3 ^c	0.2 ^e
CO		
competitive ads	0.2 ^c	0 ^e

^a Initial pressures of NO and CO 100/100 Torr. ^b Equilibrium pressure 51.6 Torr. ^c Equilibrium pressure 72.7 Torr. ^d Equilibrium pressure 60.2 Torr. ^e Equilibrium pressure 82.3 Torr.

Table V. Effects of Preadsorption of H₂O and O₂ on the Catalytic Activity for the CO-O₂ Reaction^a

catalyst	reaction rates, (mol of CO/mol of CoTPP)/min ^b		
	fresh	H ₂ O ^c	O ₂
CoTPP/TiO ₂ -120s-250	1.5	1.0	7.5 × 10 ⁻¹ ^d
CoTPP/TiO ₂ -120s-200	6.8 × 10 ⁻¹	5.3 × 10 ⁻¹	6.4 × 10 ⁻¹ ^e
CoTPP/TiO ₂ -300-200	3.0 × 10 ⁻¹	2.4 × 10 ⁻¹	3.0 × 10 ⁻¹ ^e

^a [CO]/[O₂] = 50/100 Torr, catalyst 0.2 g, at 0 °C. ^b Initial rates. ^c 0.3 mol of H₂O/mol of CoTPP was preadsorbed. ^d 0.3 mol of O₂/mol of CoTPP was preadsorbed. ^e 0.1 mol of O₂/mol of CoTPP was preadsorbed.

Their sum (1.1 mol/mol of CoTPP) coincided with the saturated amount of NO single adsorption at the same temperature as described in Table III. In contrast, NO adsorbed preferably on CoTPP/TiO₂-300-200 to suppress strongly the adsorption of CO to be nearly nil. Such results suggest that although both substrates are adsorbed commonly on the central metal ion of the complex in both catalysts, they can share the active sites on the former catalyst whereas CO is expelled by NO on the latter catalyst.

Poisons in the CO-O₂ Reaction. The effects of preadsorption of H₂O and O₂ on the catalytic activities of three catalysts for the CO-O₂ reaction are summarized in Table V. When 0.3 mol of H₂O/mol of CoTPP was preadsorbed, the catalytic activity decreased to be 70–80% of the original ones for all catalysts; however, it was completely restored by the evacuation at the temperature of each preparation condition.

The preadsorption of O₂ decreased markedly the activity of CoTPP/TiO₂-120s-250, whereas very slight or no decrease of the activity was observed on CoTPP/TiO₂-120s-200 and CoTPP/TiO₂-300-200, respectively. It is notable that the poisoning by O₂ proceeded gradually during the CO-O₂ reaction. For all catalysts, CO₂ of 100 Torr in the reactant gases caused no influence on their activities.

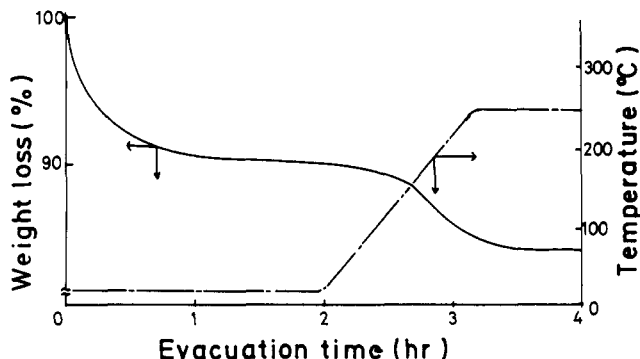
The activity loss of CoTPP/TiO₂-300-200 in the repeated CO-O₂ reaction (Table II) is suggested to be due to poisonous reaction intermediates. In fact, carbon dioxide was detected in the gas phase when the catalyst was evacuated at 200 °C after the reaction. In contrast, irreversibly adsorbed O₂ must be the major poison causing activity loss of CoTPP/TiO₂-120s-250 in the repeated reaction.

ESR Signals of the Catalysts. The catalysts exhibited ESR signals, of which *g* values and relative intensities are summarized in Table VI. The signals could be ascribed to free radical (*g* = 2.002)^{1,8,9} and Ti³⁺ (*g* = 1.935). CoTPP/

Table VI. Relative Concentrations of Free Radicals and Ti³⁺ in CoTPP/TiO₂-120s and CoTPP/TiO₂-300^a

	<i>g</i> value ^b /relative concn ^c	
	free radical	Ti ³⁺
CoTPP/TiO ₂ -120s-250	2.002/1	1.935/1.8 × 10 ⁻¹
CoTPP/TiO ₂ -120s-200	2.002/0.9	1.935/1.8 × 10 ⁻¹
CoTPP/TiO ₂ -300-200	2.002/1.7	1.935/4.5 × 10 ⁻²

^a Measured at room temp. ^b Based on Mn²⁺. ^c Relative intensity to that of free radical in CoTPP/TiO₂-120s-250.

**Figure 5.** Weight loss of CoTPP/TiO₂-120s by the evacuation from 20 to 250 °C.

TiO₂-300-200 exhibited the largest intensity of free radical signal. The intensities of the Ti³⁺ signal were very small relative to those of free radical with all catalysts, the largest intensity being observed with CoTPP/TiO₂-120s-250 and -200.

The introduction of oxygen at room temperature decreased the intensities of both free radical and Ti³⁺ very much by providing a new signal at *g* = 2.016 which is ascribed as O₂^{-•}.¹⁰ the intensity of the former signal decreased by 80% with CoTPP/TiO₂-300-200 and CoTPP/TiO₂-120s-200 and by 99% with CoTPP/TiO₂-120s-250, while the latter signal disappeared completely with all catalysts. The evacuation at room temperature restored completely the intensity of free radical with the former two catalysts; however, the complete regeneration with the latter catalyst required the evacuation at the temperature of its preparation (250 °C). The new signal at *g* = 2.016 disappeared after the evacuation at room temperature with all catalysts.

Introduction of hydrogen decreased the intensity of free radical, the most marked and smallest decreases (by 70 and 6%, respectively) being observed with CoTPP/TiO₂-300-200 and CoTPP/TiO₂-120s-250, respectively. No change of Ti³⁺ signals was observed. The evacuation at room temperature restored the intensity.

When 0.5 mol of H₂O/mol of CoTPP was adsorbed at room temperature on CoTPP/TiO₂-120s-250 and CoTPP/TiO₂-300-200, the intensities of free radicals decreased by ca. 40% on both catalysts while intensities of Ti³⁺ stayed unchanged.

Evolved Gases and Structure Change of the Complex during the Heat Treatment of CoTPP/TiO₂-120s. The weight decrease of CoTPP/TiO₂-120s in the heat treatment up to 250 °C is illustrated in Figure 5. The weight of the catalyst decreased by 10% by the evacuation at room temperature to be leveled off. Further decrease was observed by the temperature rising to be 85% of the initial value at 250 °C. The evacuated gas consisted exclusively of water up to 200 °C, where other gases (their molecular weights 44 (CO₂), 80, 95) started to evolve. A

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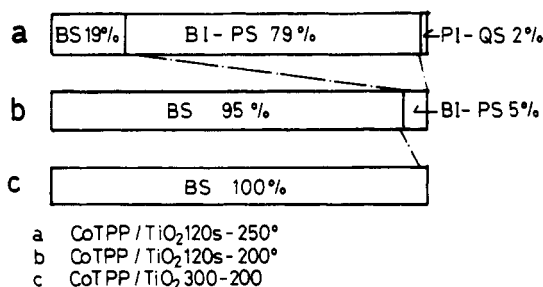


Figure 6. Solubilities of CoTPP supported on titania against several solvents: BS, benzene-soluble; BI-PS, benzene-insoluble-pyridine-soluble; PI-QS, pyridine-insoluble-quinoline-soluble.

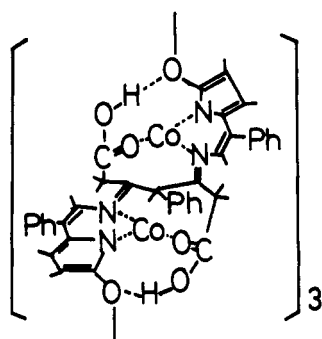


Figure 7. Estimated structure of one of the pyridine-soluble fractions.

significant change of the chemical structure of CoTPP was suggested.

Solubilities of CoTPP on the catalysts in some solvents are summarized in Figure 6. CoTPP on TiO₂-300-200 or TiO₂-120s-200 was almost completely soluble in benzene, more than 90% being extracted without any change of the structure. In marked contrast, only 20% of CoTPP supported on TiO₂-120s-250 was extracted by benzene. The major component was soluble in pyridine. Again, marked structural change during the evacuation at 250 °C is suggested.

The pyridine-soluble fraction gave weak adsorption peaks at 435, 475, and 550 nm in its visible spectrum and broad bands of low intensity due to C-H of the pyrrole structure of CoTPP in its IR spectrum. The IR spectrum of this fraction also showed a peak at 1700 cm⁻¹ assigned to be carbonyl groups. Its gel permeation chromatogram (GPC) suggested that this fraction contained at least three kinds of components of which the average molecular weight was about 1200. Silica gel chromatography suggests that this fraction consisted of more than eight compounds. One of the (8 wt % loaded CoTPP) was estimated to be a trimer of the bililvanate¹¹ like structure (Figure 7), on the basis of the following analytical characteristics: λ_{max} 433, 476, and 599 nm; IR, 1700 and 1080 cm⁻¹; Co/N ratio, 0.6; and average molecular weight, 1920 (vapor pressure osmometry (VPO)).

These observations suggest that CoTPP was oxidized into oligomers, principally dimers or trimers, through the opening of the π -conjugated ring in the ligand during the evacuating heat treatment at 250 °C.

Discussion

The remarkable catalytic activity of CoTPP/TiO₂ has been ascribed to the marked ability of supported CoTPP for the activation of CO, NO, O₂, and H₂.¹⁻³ Such an ability can be assumed to be ascribed to Co^{(2-δ)+} and free radical

on the ligand, both of which are produced by the electron transfer from TiO₂ to supported CoTPP. The former and latter sites may activate three substrates of CO, NO, O₂, and H₂, as also suggested by the present competitive adsorption study.

Three catalysts of CoTPP on TiO₂ examined in the present study exhibited some contrast behaviors in the activity preferences, reaction orders in the substrates, and manners of activity decrease. Such contrast features of the catalysts reflect their adsorption abilities against the substrates. CoTPP/TiO₂-300-200 adsorbs more hydrogen by its more free radicals than CoTPP/TiO₂-120s-250, exhibiting better catalytic activity in the NO-H₂ reaction. In contrast, CoTPP/TiO₂-120s-250 can certainly adsorb carbon monoxide in the competitive adsorption, exhibiting much higher catalytic activity in the NO-CO and CO-O₂ reactions than CoTPP/TiO₂-300-200. The reaction orders over the catalysts correctly reflect their adsorption abilities.

All of these contrast features of the catalysts should come from the detail structured of the ligand as well as supporting TiO₂ which should define the extent of electron transfer to produce the Co^{(2-δ)+} ion of CoTPP and the number of free radicals on the ligand. It is not easy to describe the structure of active catalyst species precisely at present. Nevertheless, it is of value to summarize the knowledge on their structures. The catalytically most active complex on TiO₂-120s after the evacuation at 250 °C is estimated to be a mixture of dimers and trimers, some of which have a bililvanate¹¹ structure produced through oxidative ring-opening oligomerization. TiO₂-120s alone evolves by the treatment at 250 °C a considerable amount of oxygen to form Ti³⁺ as indicated by ESR. Such structures of supporting TiO₂ and the complex appear to be most suitable for the electron transfer from the support to the central cobalt ion to exhibit the highest activation ability against CO and NO. Oxygen destroys Ti³⁺ sites of the titania surface, being a poison for the catalytic reaction which is removed by evacuation at 250 °C. In contrast, smaller conjugation in the ligand of the modified complex may not be suitable for the formation of the free radical and hence exhibits smaller ability for the adsorption and activation of hydrogen. At present, no experimental evidence is found on the activation of oxygen on the catalysts, although its reversible adsorption may take place on the central ion of CoTPP to interact with free spins on the ligand.

Such structures of both complex and TiO₂-120s are produced because of high reactivity of oxygen in TiO₂-120s, which evolves during the evacuation at 250 °C. Since the dimerized form of CoTPP has been reported when CoTPP supported on carbon is heated up to 800 °C,^{12,13} oxygen may oxidize the peripheral ligand of the complex into the dimeric and trimeric forms. Thus, the oxidative oligomerization of the complex and oxygen vacancy on the surface of TiO₂-120s were deduced. Evacuation at 200 °C is not enough to induce such modification in the complex and TiO₂-120s, no marked characteristics being brought about with CoTPP/TiO₂-120s-200 which behaves rather similarly to CoTPP/TiO₂-300-200, although slight differences due to the natures of supporting TiO₂ are still present.

The complex of CoTPP/TiO₂-300-200 keeps its structure after the evacuation at 200 °C. The properly dehydrated surface of TiO₂-300 provides some active sites on the surface such as naked titanium ions and/or the groups of

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–Ti(OH)–O– (the combination of a bidentate oxygen, $O^{-2/3}$, and a monodentate OH group, $OH^{-1/3}$, can release an electron),^{3,14} which can donate electrons to the complex to produce both $Co^{(2-\delta)+}$ ions of CoTPP and free radicals in the ligand. δ in $Co^{(2-\delta)+}$ of CoTPP/TiO₂-300-200 may be smaller than that of CoTPP/TiO₂-120s-250, probably because d-orbitals on the central Co ion may overlap with conjugated π -electrons of the ligand in CoTPP, whereas the ligand of broken conjugation in the complex altered by the treatment at higher temperature on CoTPP/TiO₂-120s-250 may never overlap with the d-orbital. However, more free radicals formed on CoTPP/TiO₂-300-200 because of the unchanged structure of the ligand to stabilize radicals, resulting in its larger catalytic and adsorption abilities against hydrogen than on CoTPP/TiO₂-120s-250.

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No retardation of oxygen is thus expected on the unreduced TiO₂ surface, whereas water can be a poison to kill the electron-donating sites of its dehydrated surface.

Although the structural difference between two TiO₂'s is still not clear at the present stage, TiO₂-120s may have more active surface to be easily reduced by evacuation than TiO₂-300. The higher reactivity of the former surface is probably due to its much lower crystallinity because of the seeding precipitation procedure and a lower calcination temperature. Such a surface of TiO₂ can evolve oxygens by the evacuation at 250 °C. The role of CoTPP in this process can be assumed according to a reverse spillover mechanism;¹⁵ i.e., oxygen atoms trapped on the TiO₂ surface migrate onto $Co^{(2-\delta)+}TPP^{*-}$ to be evolved as O₂ molecules.

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