adsorption sites for methanol. The bridged structure proposed for species I is in nice agreement with the model described by Knözinger et al.[33] for the acid–base pair sites in which dissociation occurs.

The adsorption sites for species II may be identified as cation–anion couples having a strong basic character. These sites, which have not been well characterized up to now, are also considered to be the dissociation sites of halogenated alcohols.

Registry No. CH_3OH, 67-56-1; Al_2O_3, 1344-28-1.

Remarkable Catalytic Activity of Cobalt Tetraphenylporphyrin Modified on a Titania for the Oxidation of Carbon Monoxide below Room Temperature

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CoTPP on TiO_2-120s modified at 250 °C under vacuum catalytically oxidized carbon monoxide rapidly with oxygen even at −79 °C. Its catalytic activity was incomparably higher than that of commerical Hopcalite. Comparison of its catalytic performance with those of the same catalyst or different TiO_2 supporting catalyst both evacuated at 200 °C revealed unique features of the present catalyst in terms of its oxygen adsorption, the poisoning of adsorbed oxygen, and the insolubility of the complex in benzene. Both significant structural modification of the complex and its strong interaction with properly dehydrated TiO_2-120s brought about by evacuation at 250 °C may induce such extraordinary activity.

Introduction

We have previously reported that supporting cobalt tetraphenylporphyrin (CoTPP) on a titania (giving CoTPP/TiO_2-300) provided a significant enhancement of its catalytic activity for the oxidation of carbon monoxide with nitric oxide (reduction of nitric oxide) as well as oxygen at moderate temperatures of 100[1–3] and 17 °C,[4] respectively. Such an interaction and consequently the catalytic activity are expected to be influenced very much by the subtle modification of the ligand structure[5,6] and the titania surface.[7]

We report here the extraordinarily high catalytic activity of CoTPP on a titania modified at an elevated temperature under vacuum for the oxidation of carbon monoxide below room temperature. Kinetic study may reveal some characteristics of the present catalyst system.

Experimental Section

CoTPP was synthesized by the Alder method.[8] TiO_2-120s and TiO_2-300, which were prepared by hydrolysis of titanyl sulfate and with and without seeds followed by calcination at 120 °C (240 m^2/g, 8.1 wt % SO_4) and 300 °C (BET surface 170 m^2/g, 8.3 wt % SO_4), respectively, were both provided by Titan Kogyo Co. CoTPP was impregnated onto titania by using a benzene solution to give a concentration of 5 wt %.

CoTPP/TiO_2-300 and CoTPP/TiO_2-120s, thus prepared, were evacuated (2×10^{-3} torr) at 200 or 250 °C for 2 h before the reaction (CoTPP/TiO_2-300-200 and CoTPP/TiO_2-120s-250, respectively). Hopcalite (MnO_2 60%, CuO 40%), a well-known catalyst of the highest activity for the oxidation of CO, was obtained from Nakarai Co. It was evacuated at 250 °C for 3 h before the reaction to exhibit the largest activity.

The catalytic reaction was carried out below 19 °C, using a circulation reactor (volume, 800 mL; circulation rate, 500 mL/min) with a fixed catalyst bed through which the reaction gases passed. The catalyst (0.2 g) was diluted with carborundum (1.0 g) in the bed to release the heat of reaction which was very essential to obtain the correct rate. Partial pressures of CO and O_2 were 5 and 10 cmHg, respectively. The gases were analyzed by a gas chromatograph (Porapak Q 2m, at room temperature for CO_2, Molecular Sieves 13x 2m, at room temperature for CO and O_2). Reaction rates were defined as initial rates of the CO_2 formation within 20% CO conversion, where experimental errors were within ±3%.

TABLE I: Catalytic Activities of Various Catalysts[a]

catalyst	reaction rate[b] 19 °C	0 °C	−79 °C
CoTPP/TiO_2-120s-250	$1.6 \times 10^{-1}/2.2$	$1.1 \times 10^{-1}/1.5$	$2.3 \times 10^{-2}/0.3$
CoTPP/TiO_2-120s-200		$2.2 \times 10^{-2}/0.3$	no reaction
CoTPP/TiO_2-300-200		$7.4 \times 10^{-3}/0.1$	no reaction
Hopcalite		$7.4 \times 10^{-3}/$	no reaction

[a] Catalyst/carborundum = 0.2 g/1 g, P_{CO} = 5 cmHg, P_{O_2} = 10 cmHg. The rate observed at conversions of less than 20% in the first run. [b] (mmol of CO_2/g of catalyst)/mol of CO_2–CoTPP·min).

Results

Catalytic Activities of CoTPP on Titanias and Commercial Hopcalite at Some Temperatures below Room Temperature. Catalytic conversion of carbon monoxide over CoTPP on titanias and commercial Hopcalite at 0 °C are compared in Figure 1, where the formation of carbon dioxide and consumption of carbon monoxide in the first catalytic run are illustrated. All catalysts examined showed significant activities to produce carbon dioxide stoichiometric to disappearence of carbon monoxide at this temperature. The formation rates of CO_2 were very rapid at the initial stage of the reaction (within 15 min) and became slower gradually

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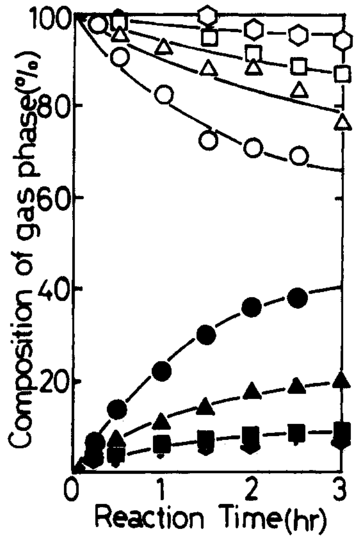

Figure 1. Catalytic activity of CoTPP's and commercial Hopcalite at 0 °C. P_{CO} = 5 cmHg, P_{O_2} = 10 cmHg, catalyst/carborundum = 0.2 g/1.0 g: (○, ●) CoTPP/TiO_2-120s-250; (△, ▲) CoTPP-TiO_2-120s-200; (□, ■) CoTPP/TiO_2-300s-200; (⬡, ⬢) Hopcalite (250 °C 3 h evacuation); open symbols, CO; filled symbols, CO_2.

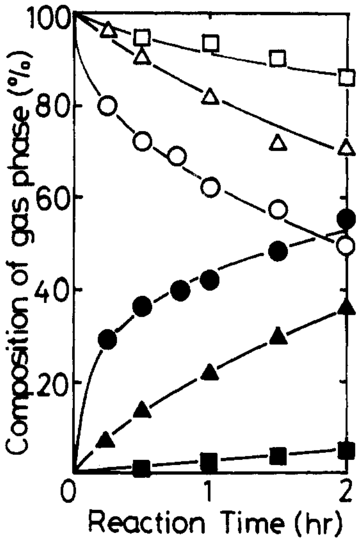

Figure 2. Catalytic activity of CoTPP/TiO_2-120s-250 at several reaction temperatures. P_{CO} = 5 cmHg, P_{O_2} = 10 cmHg, catalyst/carborundum = 0.2 g/1.0 g: (○, ●) 19 °C; (△, ▲) 0 °C; (□, ■) −79 °C; open symbols, CO; filled symbols, CO_2.

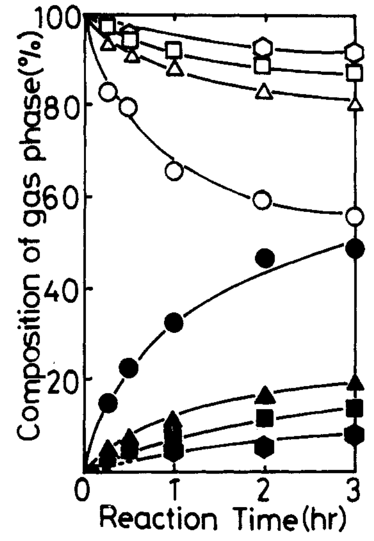

Figure 3. Catalytic activity of CoTPP/TiO_2-120s-250 in repeated runs at 0 °C. P_{CO} = 5 cmHg, PO_2 = 10 cmHg, catalyst/carborundum = 0.2 g/1.0 g: (○, ●) first run; (△, ▲) second run; (□, ■) third run; (⬡, ⬢) fourth run; open symbols, CO; filled symbols, CO_2.

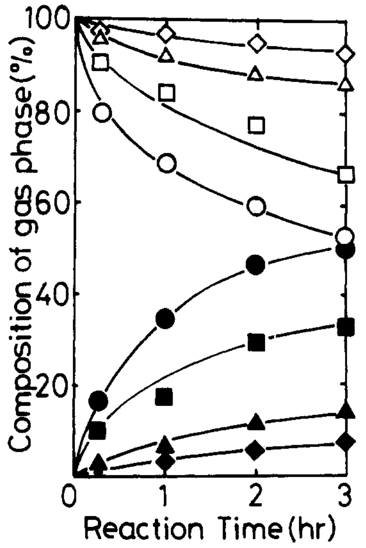

Figure 4. Recovery of catalytic activity of CoTPP/TiO_2-120s-250. P_{CO} = 5 cmHg, P_{O_2} = 10 cmHg, catalyst/carborundum = 0.2 g/1.0 g, evacuation conditions before the catalytic reaction: (◆, ◇) 100 °C, 2 h; (△, ▲) 150 °C, 2 h; (□, ■) 200 °C, 2 h; (○, ●) 250 °C, 2 h; open symbols, CO; filled symbols, CO_2.

to be about one third of the initial values on all catalysts. By comparing the yield of CO_2 after 3 h of reaction among the catalysts, we found that CoTPP/TiO_2-120s-250 exhibited the highest catalytic activity which was six times larger than that of commercial Hopcalite. The activity was twice high as that of the same catalyst evacuated at 200 °C. TiO_2-120s was a better support for CoTPP than TiO_2-300 when the evacuation conditions (200 °C, 2 h) before the reaction were same, showing a three times larger activity. The activity of CoTPP/TiO_2-300-200 was same to that of Hopcalite at this temperature.[3]

The catalytic activities of CoTPP/TiO_2-120s-250 at 19 and −79 °C are illustrated in Figure 2. It should be noted that the reaction proceeded even at −79 °C. The higher reaction temperature provides a larger rate of carbon monoxide consumption, the activation energy being calculated as 2.3 kcal/mol. Less carbon dioxide was found in the gas phase at −79 °C than expected from the disappearance of carbon monoxide, indicating considerable adsorption of the gas as described later.

The activities of the catalysts examined in the present study are summarized in Table I where the initial rates of carbon dioxide formation per gram of catalyst were selected to be their measures. The site–time yields over supported CoTPP are also included in Table I, where all CoTPP molecules are assumed to contribute to the catalytic activity since they adsorbed carbon monoxide very rapidly. The highest activity of CoTPP/TiO_2-120s-250 was clearly indicated at any temperature below room temperature. It must be noted that its site–time yield was as high as 1.5 mol of CO_2/(mol of CoTPP·min) within the initial 15 min when 22 molecules of carbon dioxide were produced on one molecule of CoTPP, indicating its excellent catalytic performance. After 15 min, the reaction rate decreased gradually with increasing the reaction time, the turnover number, reacted carbon monoxide (i.e. carbon dioxide formed, mol) divided by CoTPP (mol) on CoTPP/TiO_2-120s-250, reaching to 65 by 3 h. Site–time yields and turnover numbers were 0.3, 32 and 0.1, 12, respectively, when CoTPP was supported on TiO_2-120s-200 and TiO_2-300-200. Thus, the kind of titania and evacuation conditions influenced very much the catalytic activity of the supported CoTPP for the oxidation of carbon monoxide.

Catalytic Activity of CoTPP/TiO_2-120s-250 in the Repeated Runs. The catalytic activities of CoTPP/TiO_2-120s-250 in the repeated runs at 0 °C are illustrated in Figure 3, where the catalyst was evacuated at 0 °C for 1 h prior to repeating the reaction. The rate decreased sharply to one third in the second run, and then

TABLE II: Adsorption[a] of CO, O_2, and CO_2 on CoTPP/TiO_2-120s-250

adsorptive	run 1	run 2[b]	run 3[b]	run 4[c]
CO	0.83	1.83	1.83	1.83
O_2	0.31	0.17	0.14	0.31
CO_2	2.30	2.30	2.30	2.30

[a] Catalyst: 1 g, at 0 °C; equilibrium pressure: 5 cmHg; mole/mole of CoTPP. [b] Evaluated at 0 °C for 1 h before the adsorption. [c] Evacuated at 250 °C for 2 h before the adsorption.

TABLE III: Effects of Preadsorption on the Catalytic Activity of CoTPP/TiO_2-120s-250

adsorbate	activity[a]	adsorbate	activity[a]
none	1.1×10^{-1}	O_2[d]	7.7×10^{-2}
CO[b]	1.1×10^{-1}	O_2[e]	5.5×10^{-2}
CO_2[c]	1.1×10^{-1}	O_2[f]	5.3×10^{-2}

[a] At 0 °C, mmol/(g of catalyst. min). The catalytic activity was observed after evacuation at 0 °C. [b] CO: 5 cmHg. [c] CO_2: 5 cmHg. [d] O_2: 10 cmHg. The adsorption was continued for 0.5 h before evacuation at 0 °C. [e] Same as footnote *d* except for adsorption for 1 h. [f] Same as footnote *d* except for adsorption for 3 h.

TABLE IV: Reactivity of Irreversibly Adsorbed Oxygen on CoTPP/TiO_2-120s-250 at 0 °C[a]

adsorption time,[b] h	CO adsorbed,[c] mol/mol of CoTPP	CO_2 produced,[d] mol/mol of CoTPP
no adsorption	1.8	
0.5	0.61	0.14
3	0.48	0

[a] Introduced oxygen 10 cmHg, 0.31 mol/mol of CoTPP was adsorbed. [b] Adsorption time before the evacuation and introduction of carbon monoxide at 0 °C. [c] Amount of adsorbed carbon monoxide. [d] Amount of produced carbon dioxide while carbon monoxide was present.

gradually in the successive runs. The evacuations below 250 °C restored only a part of the initial activity according to the temperature as shown in Figure 4. Complete recovery of the initial activity required evacuation at 250 °C, suggesting that some poisons may block the active site.

Kinetics and Adsorption on CoTPP/TiO_2-120s-250. The reaction orders in carbon monoxide and oxygen were calculated first and zero, respectively, at 0 °C on CoTPP/TiO_2-120s-250.

The adsorption of carbon monoxide and oxygen on CoTPP/TiO_2-120s-250 at 0 °C is summarized in Table II, where adsorbed gases are described in mole per mole of CoTPP. Carbon monoxide and oxygen adsorbed rapidly on the catalyst, almost to saturation within 1 min, whereas carbon dioxide did so more slowly. Thus, the major parts of supported CoTPP are suggested to contribute to the catalytic activity.

Roughly speaking, two molecules of carbon monoxide, carbon dioxide, and 0.3 molecules of oxygen were adsorbed on one molecule of CoTPP on the titania in the first adsorption. The same amount of carbon monoxide was adsorbed in the second and third runs after evacuation at 0 °C for 1 h, indicating the reversibility of its adsorption at this temperature. Adsorption of carbon dioxide was similarly reversible. In contrast, the amount of oxygen adsorption decreased to about one-half in the second run after evacuation at 0 °C. Some further decrease of oxygen adsorption was observable in the third run. The evacuation at 250 °C, however, restored the initial adsorption of oxygen. Thus, reversible adsorption of oxygen was only one third of total adsorption at 0 °C, although irreversibly adsorbed oxygen at 0 °C desorbed at 250 °C under vacuum.

The influences of preadsorption of carbon monoxide, carbon dioxide, and oxygen on the catalytic activity of CoTPP/TiO_2-120s-250 at 0 °C are summarized in Table III, where the catalyst was evacuated at 0 °C prior to the reaction. Both carbon dioxide and monoxide gave no effects on the catalytic activity when they are preadsorbed. Rather interesting deactivation features were observable with the preadsorption of oxygen. The catalytic activity was significantly decreased by the preadsorption of oxygen: the extent of decrease was strongly dependent upon the adsorption time, although the adsorption appeared to be apparently completed within 30 min. The catalytic activity after oxygen adsorption for 0.5 h was two-thirds of original. Longer adsorption times of 1 h decreased the activity to one-half of original. The rate is comparable to that observed in the second run of the fresh catalyst. Adsorption for 3 h decreased the activity slightly further.

The reactivities of irreversibly adsorbed oxygen on CoTPP/TiO_2-120s-250 observed with carbon monoxide at 0 °C are summarized in Table IV, where the adsorption time was varied from 0.5 to 3 h before the introduction of carbon monoxide. Without adsorbed oxygen, 1.8 molecules of carbon monoxide was adsorbed on one molecule of CoTPP on titania without any oxydation. When the adsorption time of oxygen was 0.5 h, the introduction of carbon monoxide produced 0.14 molecule of carbon dioxide per CoTPP molecule and 0.61 molecule of carbon monoxide adsorbed on CoTPP. Since 0.31 molecule of oxygen was adsorbed, only one-fourth reacted with carbon monoxide. An adsorption time of 3 h reduced the amounts of oxidized and adsorbed carbon monoxide to nil and 0.48 molecules per CoTPP, respectively.

Such results indicate that two kinds of adsorbed oxygen species are present on CoTPP/TiO_2-120s-250; one species which is formed rapidly is reactive, whereas the other which appears to be slowly formed from the former is nonreactive and retards the adsorption and oxidation of carbon monoxide.

Extraction from CoTPP/TiO_2-120s-250 and the Activities of Extracted Residues. 20, 98, and 100% of the supported complex on CoTPP/TiO_2-120s-250 were extracted at room temperature with benzene, pyridine, and quinoline, respectively. In contrast, almost all of the complex on TiO_2-300-200 was extracted with benzene.[2] The major portion of CoTPP on TiO_2-120s was, thus, converted to be insoluble in benzene but soluble in quinoline during the evacuation at 250 °C. The atomic ratios and molecular weights of CoTPP and the benzene, pyridine, and quinoline extracts are summarized in Table V. CoTPP and the benzene extract exhibited essentially the same ratios, suggesting that the benzene extract maintains the structure as reported previously.[2] The pyridine and quinoline extracts lost some carbons, suggesting a considerable change of ligand structure, although each cobalt ion still carried four nitrogen atoms. The molecular weight of the benzene extract was essentially the same as that of CoTPP, whereas that of the pyridine extract was roughly twice that of CoTPP. Some dimerization of the complex is suggested.

The catalytic activity of the benzene extraction residue was essentially the same as that of the original CoTPP/TiO_2-120s-250, although 20% of the supported CoTPP was extracted. The pyridine extraction lost the major activity, suggesting that the extract is the major catalytic species of CoTPP/TiO_2-120s-250.

TABLE V: Atomic Ratio of CoTPP and Extracts and the Activity of Extracted Residues from CoTPP/TiO_2-120s-250

		atomic ratio					
	extraction yield, %	C	H	N	Co	mol wt	catalytic activity[a]
CoTPP		44	28	4	1	672[b]	1.1×10^{-1}[d]
benzene extract	20	43	29	4	1	700[c]	1.1×10^{-1}
pyridine extract	79	42	28	4	1	1106[c]	3.5×10^{-2}
quinoline extract	1	40	28	4	1		5.1×10^{-4}

[a] Activity of residue (mmol/(g of catalyst-min)). For conditions see Table I. [b] Calculated from formula 690 was obtained by vapor pressure osmometer. [c] Observed with a vapor pressure osmometer. [d] Activity of CoTPP/TiO_2-120s-250.

The last activity of the catalyst was removed completely by extraction with quinoline.

More than 99% of supported CoTPP was extracted with benzene without a structural change for CoTPP/TiO_2-120s-200.

Discussion

CoTPP/TiO_2-120s exhibited an extraordinarily high catalytic activity for the oxidation of carbon monoxide with oxygen at temperatures as low as −79 °C (0.3 mol of CO_2/(mol of CoTPP·min)) by evacuating it at 250 °C. Such a high activity incomparable with those of CoTPP/TiO_2-300 or CoTPP/TiO_2-120s-200 should originate from the intimate interaction of the catalytic species of CoTPP or its derivatives with the supporting titania of a particular state. The partially reduced Co^{2+} ion of CoTPP may be produced on TiO_2 by evacuation at 250 °C. Such an ion can coordinate to carbon monoxide through back-donation to enrich the valence electrons on the carbon atom and enhance the abstraction of the oxygen atom from the adsorbed oxygen molecule as postulated in previous papers.[1-3]

Such a back-donation and activation ability of the Co^{2+} ion should be very much influenced by the properties of the TiO_2 surface as well as the ligand structure since the partially reduced Co^{2+} ion is produced by electron transfer from a particular titania to the CoTPP. Evacuation treatment at 250 °C made the majority of the CoTPP on TiO_2-120s insoluble in benzene but soluble in quinoline. The benzene-extractable complex is indifferent to the present level of catalytic activity. The structure of extracted complex appeared to be considerably modified, based on the chemical analysis and molecular weight. Dimerization of the peripheral ligand with some loss of phenyl groups is suggested. Such a modification is brought about thermally under vacuum at a particular temperature of 250 °C. Similar thermal modifications of CoTPP were reported on the carbon surface,[5,6] although a much higher temperature was required on the carbon surface. Higher catalytic activities of some poly(phthalocyanine)s have been reported in some oxidation and reduction reactions.[9-12]

Evacuation treatment at this temperature may also induce most naked titanium ions surrounded by a particular number of hydroxyl groups on the titania surface as reported by Enriquetz and Faisoard.[13] Such sites are more suitable for electron donation, as well-documented on the alumina surface where suitable dehydration provides the strongest acidity.[14]

CoTPP/TiO_2-120s-250 can adsorb both carbon monoxide and oxygen at 0 °C. The reaction orders of first and zero in carbon monoxide and oxygen, respectively, may suggest that the reaction may take place between oxygen of saturated adsorption and carbon monoxide highly activated on CoTPP. Although the adsorption site of oxygen is not definite at present, it may be on the titania surface in the vicinity of CoTPP, being different from the site which interacts with CoTPP.

In spite of the major reaction path described above, the catalytic activity decreased in the repeated runs unless the catalyst was evacuated at 250 °C. Oxygen is first adsorbed on titania to be active; however, it is transferred to the reduced sites of supporting titania (sites interacting with CoTPP) to be irreversibly adsorbed below 250 °C. Such irreversibly adsorbed oxygens must lose their reactivity with carbon monoxide. Furthermore, these oxygens also decrease the electron-donating activity of the support to decrease the catalytic and adsorption activities of supported CoTPP against carbon monoxide. The oxygens are removed by evacuation at 250 °C, regenerating the initial high activity.

Registry No. CoTPP, 14172-90-8; TiO_2, 13463-67-7; CO, 630-08-0; O_2, 7782-44-7.

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Excited Dye Reactions with Damaged Zinc Oxide[†]

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Electrochemical studies of electron exchange between dyes and the conduction band of ZnO are reported, emphasizing the effect of dislocation levels (surface damage) on the exchange. It is found with rhodamine B that anodic electron injection from the excited dye is enhanced substantially by the presence of dislocations. Cathodic electron flow to the ground state of the rhodamine B (while the dye is excited) is also substantial in the presence of dislocations. In the case of rose bengal, the anodic electron injection from the excited dye and the cathodic electron flow to the ground state of the excited dye are each increased, but only moderately, by dislocation levels. The results are interpreted as suggesting that the energy levels of the dislocations act as transfer levels for electron flow in either direction between the conduction band and those surface levels of the dyes located in the bandgap region.

Introduction

In an earlier contribution[1] the effect of damage (surface dislocation loops) on electron transfer from the n-type zinc oxide (0001) face to various ions in solution was studied. It was observed that for energy levels well below the conduction band a substantial increase in current was observed associated with the damage. It was suggested that electrons could move through dislocation levels to the surface, where they could, in an isoenergetic electron-transfer process, transfer to the energy levels in the solution. This provided some clarification on the role of dislocation levels in electrode reactions.

For many years studies have been made of the reaction of excited dyes on zinc oxide.[2,3] The interest was undoubtedly

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