A Kinetic Study on Reduction of Nitric Oxide over Cobalt Tetraphenylporphyrin Supported on Titanium Dioxide

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The catalytic reduction and decomposition of nitric oxide and nitrous oxide over cobalt tetraphenylporphyrin supported on TiO_2 (Co–TPP/TiO_2) were investigated kinetically and mechanistically in the reaction temperature range of 50 to 150°C, and reveal a high catalytic activity brought about by supporting on titanium dioxide. The kinetic equation for the reduction of nitric oxide with hydrogen over Co–TPP/TiO_2 ($V = k \times P_{NO}^{-0.9} P_{H_2}^{0.6}$) suggested that the surface reaction between nitric oxide adsorbed strongly on the cobalt ion and hydrogen adsorbed dissociatively on the porphyrin ring is the rate-determining step. The selective formation of nitrous oxide in the initial stage of the reaction and its successive transformation to molecular nitrogen were explained in terms of the stronger adsorption of nitric oxide. Decomposition of nitric oxide and nitrous oxide also proceeded over this catalyst, producing nitrous oxide and molecular nitrogen, respectively. The residual oxygen produced on Co–TPP may be transferred to the support to a certain limit. The characteristic activity of Co–TPP/TiO_2 can be ascribed to the drastic modification in the electronic configuration of the cobalt ion, as well as the porphyrin ring, induced by the electron transfer from the support.

INTRODUCTION

Considerable efforts on NO_x abatement have been made in various countries to meet present or anticipated regulations (*1*). Selective reduction of NO_x by an active catalyst at low temperatures is still a desirable goal. A number of catalytic systems mainly composed of oxides have been reported (*2*). The present authors have reported in previous papers (*3*) the catalytic activity of macrocyclic cobalt or nickel complexes such as phthalocyanines in reduction of NO_x with hydrogen. The most interesting observation is that cobalt tetraphenylporphyrin (Co–TPP) exhibited a remarkable enhancement of activity around 100°C by supporting it on TiO_2 (abbreviated as Co–TPP/TiO_2), no reaction being observable on Co–TPP alone. The enhancement appeared to be related to electron transfer from the oxide to the complex, which was spectroscopically revealed (*4*).

In the present paper, a kinetic study of the reduction was performed with respect to reaction orders and adsorption of reactant gases to provide a reaction mechanism which could explain the excellent activity of Co–TPP/TiO_2. During the study of adsorption of nitric oxide in the absence of hydrogen, the spontaneous decomposition of nitric oxide into nitrous oxide and nitrogen was found to proceed without hydrogen over the catalyst. The latter interesting reaction was also studied, although it was a rather slow one.

EXPERIMENTAL

Catalyst

Co–TPP was synthesized according to the method of Adler *et al.* (*5*). The purity of the complex was examined by elemental

analysis and uv spectroscopy (Shimazu UV-202) [calcd: C 78.70%, N 8.35%, H 4.17%; obsd: C 78.35%, N 8.31%, H 4.27%; $\lambda_{max}(\epsilon \times 10^{-3})$: 528.5 nm (15.9), 413 nm (249.3)].

Titanium dioxide was supplied by Titan Industry, Ube, Japan. It was prepared from titanium oxysulfate and calcined at 300°C. The BET surface area was 156 m²/g.

TiO_2 was added to a red-purple solution of Co–TPP in benzene and stirred at room temperature for several hours. By removing the solvent under reduced pressure, a green slurry of Co–TPP/TiO_2 (5 wt% Co–TPP) was prepared. Metal-free tetraphenylporphyrin supported on TiO_2 (H_2–TPP/TiO_2) was prepared in the same manner.

Procedure

All catalytic reactions were investigated by a conventional closed-circulation reactor (volume: ca. 800 ml). The catalyst amount and the circulating rate were 4 g and ca. 500 ml/min, respectively. The products (N_2O and N_2) and the reactant (NO) were analyzed by a gas chromatograph. Since no ammonia was present in the product, the amount of NO adsorbed during the reaction was calculated from the material balance, taking account of the pressure change detected by a mercury manometer. Partial pressures of nitric oxide and hydrogen were varied in the ranges 5.5–40.5 and 100–500 Torr, respectively, for the kinetic study at 100°C. The conversion and yields were reproduced within 10% error. Adsorption and decomposition of nitric oxide and nitrous oxide were studied with the same apparatus in the absence of hydrogen. Detailed procedures and analyses of the reactions were described in a previous paper (6).

The adsorption of hydrogen was observed volumetrically with a glass apparatus (dead space: 33.4 ml) equipped with a mercury manometer and connected to a vacuum line and gas reservoirs. After the adsorbent (1 g) was evacuated at a fixed temperature for 1 hr, hydrogen (500 Torr) was brought into contact with the adsorbent, the hydrogen uptake being monitored by a mercury manometer.

RESULTS

Kinetic Study of Nitric Oxide Reduction with Hydrogen over Co-TPP/TiO₂

The rates of reduction of nitric oxide with hydrogen over Co–TPP/TiO_2 at 100°C under variable pressures of nitric oxide (5.5–40.5 Torr) at a fixed hydrogen pressure (400 Torr) and under variable hydrogen pressure (100–500 Torr) at a fixed pressure of nitric oxide (20 Torr) were observed. Nitrous oxide was the only nitrogen-containing product at the early stage of the reaction where the kinetics of the reaction were studied, although nitrogen was produced at a later stage, indicating a successive transformation, $NO \rightarrow N_2O \rightarrow N_2$.

Increasing hydrogen pressure accelerated the formation of nitrous oxide; however, the adsorption rate and level of nitric oxide were slightly decreased by the increasing hydrogen pressure. The logarithmic plots of the rate for the formation of nitrous oxide against the hydrogen pressure indicated a reaction order of 0.6 in hydrogen. The latter result may mean that hydrogen is dissociatively adsorbed. No essential change of NO adsorption level may imply that the site for hydrogen adsorption differs from that for nitric oxide, or that the adsorption of nitric oxide is strong enough to be slightly influenced by the excess amount of hydrogen.

Increasing pressure of nitric oxide decreased the rate for the formation of nitrous oxide, although the adsorption level of the reactant gas was a little increased. The logarithmic plots of the rate vs the pressure of nitric oxide indicated a reaction order of -0.9 in nitric oxide for the formation of nitrous oxide.

On the basis of these results, the rate equation for the formation of nitrous oxide is

TABLE 1

Reactivities of NO and N$_2$O with and without H$_2$ over Co–TPP/TiO$_2$

Run	Type of reaction[a]	Reaction temp. (°C)	NO → N$_2$O,N$_2$		N$_2$O → N$_2$	
			(N$_2$O)[b]	(N$_2$)[b]	(N$_2$O)[c]	(N$_2$)[b]
1	NO–H$_2$	50	2.4×10^{-3}	1.0×10^{-3}	—	—
2	NO–H$_2$	100	4.6×10^{-3}	0	—	—
3	NO–H$_2$	150	3.2×10^{-2}	0	4.2×10^{-2}	$4.2 \times 10^{-2\,d}$
4	N$_2$O–H$_2$	150	—	—	5.2×10^{-2}	4.8×10^{-2}
5	N$_2$O–NO–H$_2$	150	3.3×10^{-2}	0	8.0×10^{-2}	$6.9 \times 10^{-2\,d}$
6	NO	100	1.2×10^{-3}	0.6×10^{-3}	—	—
7	NO	150	2.1×10^{-2}	2.1×10^{-3}	—	—
8	N$_2$O	100	—	—	4.8×10^{-3}	1.5×10^{-3}
9	N$_2$O	150	—	—	2.8×10^{-2}	2.6×10^{-2}

[a] For details of the reaction conditions refer to Figs. 1–3.

[b,c] Consumption rate (c) and formation rate (b) are in mmol/g-cat. hr units. These rates (V) were calculated by the equation

$$V = \frac{(x/100) \cdot (1000aP_{NO}/RT)}{t \cdot W} \text{ (mmol/g-cat. hr)},$$

x: NO conversion or yields of N$_2$O or N$_2$ (%),
a: volume of reactor,
P_{NO}: initial pressure of NO,
t: reaction time,
W: catalyst weight.

[d] The rates were observed after all nitric oxide in the system was reduced.

$$V_{N_2O} = 7.3 \times 10^{-4} P_{H_2}^{0.6} P_{NO}^{-0.9}$$
$$\text{(mmol/g-cat. hr). (1)}$$

The rates of NO reduction to N$_2$O at various temperatures are summarized in Table 1. The apparent activation energy for the formation of nitrous oxide was calculated from the rates to be 9.6 kcal/mol. It should be noted that the reduction of nitrous oxide took place only after no nitric oxide remained, although the rates for both reactants were similar.

Adsorption Measurements of Nitric Oxide and Hydrogen

The amounts of adsorbed nitric oxide over Co–TPP/TiO$_2$ during the reaction of nitric oxide with and without hydrogen in the circulating reactor are summarized in Table 2. At 50°C, more than one molecule of nitric oxide was adsorbed on each molecule of Co–TPP on TiO$_2$ before any significant reaction of nitric oxide, suggesting that

TABLE 2

Adsorption of Nitric Oxide over Co–TPP/TiO$_2$[a]

Reaction temp. (°C)	Adsorbed NO (μmol/g-cat.)		Mole ratio of adsorbed NO/Co–TPP	
	Without H$_2$[b]	With H$_2$[c]	Without H$_2$[b]	With H$_2$[c]
50	116.6	101.1	1.56	1.36
100	55.7	48.4	0.75	0.65
150	56.9	48.4	0.76	0.65

Note. Catalyst = 4 g; P_{NO} = 20 Torr.

[a] No adsorption of nitric oxide was observed on TiO$_2$ at 150°C under the present conditions.

[b] Adsorption level 2 hr after the introduction of nitric oxide, when no significant decomposition took place.

[c] Adsorption level 30 min after the introduction of nitric oxide, when no significant reduction took place except for 150°C.

a part of nitric oxide coordinates in twin or dimer form. Since TiO_2 alone adsorbed nitric oxide to a much smaller extent compared to the adsorption by $Co–TPP/TiO_2$, the major part of nitric oxide is believed to be adsorbed on the Co–TPP. At 100 and 150°C, less than one molecule of nitric oxide was adsorbed on each molecule of Co–TPP. Although adsorption of nitric oxide was slightly decreased in the presence of hydrogen as described above, the number of adsorbed nitric oxide molecules on a Co–TPP molecule was essentially unchanged regardless of the presence of hydrogen.

Significant adsorption of hydrogen was observable at room temperature on $Co–TPP/TiO_2$ and $H_2–TPP/TiO_2$, as shown in Table 3. The amount of adsorbed hydrogen on $Co–TPP/TiO_2$ increased with higher evacuation temperatures. It should be noted that $H_2–TPP/TiO_2$ evacuated at 100°C for 1 hr also adsorbed an amount of hydrogen comparable to that adsorbed by $Co–TPP/TiO_2$ at room temperature. TiO_2 showed no adsorption activity for hydrogen even after evacuation at the elevated temperature. Adsorption on metallic cobalt can be ruled out since $H_2–TPP/TiO_2$ can adsorb and no adsorption was observed on burnt $Co–TPP/TiO_2$ which lost the ligand. These facts may indicate that the porphyrin ring electronically modified by titanium dioxide provides an adsorption site for hydrogen. It should be mentioned that Co–TPP without titanium dioxide has no capacity for hydrogen adsorption.

Catalytic Activity of Co–TPP/TiO₂ for Reduction of Nitrous Oxide

The catalytic activities of $Co–TPP/TiO_2$ for the reduction of nitrous oxide with hydrogen at 150°C, with nitric oxide in the gas phase, are shown in Fig. 1.

In the case without nitric oxide in the gas phase, nitrous oxide was quantitatively converted into molecular nitrogen at the rate of 4.8×10^{-2} mmol/g-cat. hr at 150°C, which is comparable to the rate of molecu-

TABLE 3

Adsorption of Hydrogen at Room Temperature (r.t.) after Evacuation at Several Temperatures

Adsorbent	Evacuation temp. (°C)	Adsorbed H_2 (μmol/g-cat.)	Adsorbed H_2 (mol H_2/mol TPP)
$Co–TPP/TiO_2$	r.t.	0.4	0.005
	100	6.1	0.082
	200	19.6	0.263
$H_2–TPP/TiO_2$	100	9.0	0.111
TiO_2	r.t.	0.0	—
	200	0.4	—

Note. H_2: 500 Torr. One gram of adsorbent was evacuated for 1 hr at evacuation temperature. The amount of adsorption was measured 2 hr after the introduction of hydrogen.

lar nitrogen formation through nitrous oxide derived from nitric oxide at 150°C after all nitric oxide reacted. The difference in the rates of N_2O consumption and N_2 formation (Table 1) may correspond to the adsorption of N_2O, which is considerably smaller than that of nitric oxide. Addition of nitric oxide in a quantity twice the amount of nitrous oxide prohibited the formation of molecular nitrogen completely,
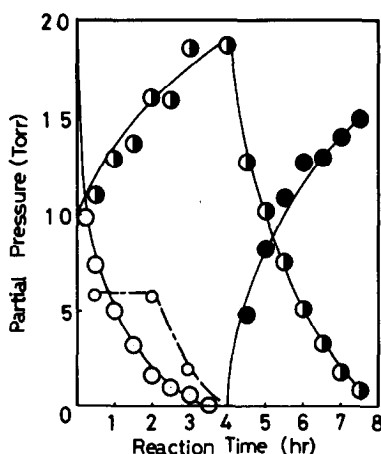

FIG. 1. Reduction profile of coexisting NO and N_2O with H_2 over $Co–TPP/TiO_2$ at 150°C. Initial pressure: $P_{NO} = 20$ Torr, $P_{N_2O} = 10$ Torr, $P_{H_2} = 600$ Torr. O——O, NO; O--O, adsorbed NO; ◑——◑, N_2O; ●——●, N_2.

simply increasing the concentration of nitrous oxide in the gas phase at the rate of 3.3×10^{-2} mmol/g-cat. hr, which is comparable to that without nitrous oxide. The amount of adsorbed nitric oxide was not affected by the presence of nitrous oxide. Nitrous oxide started to react only after all nitric oxide was consumed. Thus, the preferred reactivity of nitric oxide on Co–TPP/TiO₂, causing the successive transformation of NO → N₂O → N₂, is ascribed to its strong adsorption, in spite of their similar reactivities. Larger rates at higher partial pressures of nitrous oxide indicate a positive reaction order in the reactant.

Decomposition of Nitric Oxide in the Absence of Hydrogen over Co–TPP/TiO₂

Table 1 shows the reaction rates for the decomposition of nitric oxide on Co–TPP/TiO₂ in the absence of hydrogen at 100 and 150°C. The reaction profile of nitric oxide at 150°C is illustrated in Fig. 2. At both reaction temperatures, considerable decreases of nitric oxide in the gas phase were observed, yielding nitrous oxide and molecular nitrogen in addition to its adsorption. The rates of nitrous oxide formation were 1.2×10^{-3} mmol/g-cat. hr at 100°C and 2.1×10^{-2} mmol/g-cat. hr at 150°C, respectively, being roughly one-fourth and two-thirds of those observed with hydrogen at the same reaction temperatures. The activation energy was 17.9 kcal/mol. A slow but distinct production of molecular nitrogen from the initial stage of the reaction should be noted, being in contrast to the complete consecutive reactions in the presence of hydrogen. The rates of nitrogen formation at 100 and 150°C were 0.6×10^{-3} and 2.1×10^{-3} mmol/g-cat. hr, respectively.

The rate of the oxygen produced from the reacted nitric oxide is to be studied. Neither molecular oxygen, nitrogen dioxide, carbon dioxide, carbon monoxide, nor water was detected in the gas phase, indicating that the residual oxygen remains on the cat-
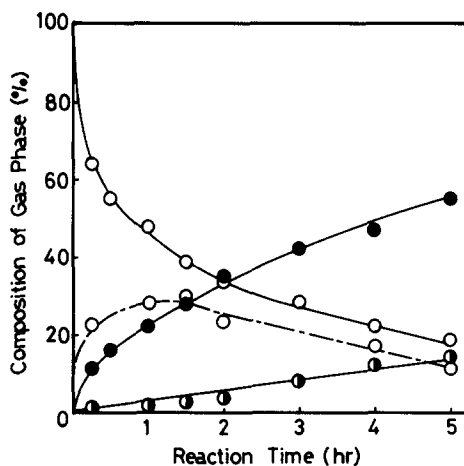

FIG. 2. Decomposition profile of NO over Co–TPP/TiO₂ at 150°C. Initial pressure of NO is 20 Torr. O——O, NO; O--O, adsorbed NO; ●——●, N₂O; ◑——◑, N₂.

alyst. Some preliminary trials using Fourier transform infrared spectroscopy failed to detect the adsorbed oxygen species. The number of reacted NO producing N₂O and N₂ over 1 mol of Co–TPP was 2.4 at 150°C by 5 hr. The number was increased up to 12 (0.5 mol/hr) by 24 hr at this temperature when the initial mole ratio of NO/Co–TPP was 26. The rate for the decomposition of nitric oxide during the second run with the same catalyst at 150°C after the evacuation at the reaction temperature was almost the same as that of the first run, indicating recovery of the active site for the decomposition.

Decomposition of Nitrous Oxide in the Absence of Hydrogen over Co–TPP/TiO₂

Decomposition of nitrous oxide in the absence of hydrogen on Co–TPP/TiO₂ proceeded when the initial pressure of nitrous oxide and reaction temperature were 10 Torr and 150°C, respectively. Nitrous oxide yielded molecular nitrogen at this temperature without hydrogen a little more quickly $(2.6 \times 10^{-2}$ mmol/g-cat. hr) than nitric oxide which gave the product via nitrous oxide $(2.1 \times 10^{-2}$ mmol/g-cat. hr). This fact suggests that the successive transformation of

nitrous oxide into molecular nitrogen is considerably retarded by nitric oxide as observed in the reaction in the presence of hydrogen, although the extent of retardation is smaller without hydrogen as indicated by the distinct formation of molecular nitrogen (Fig. 2). No molecular oxygen was detected in the gas phase of this reaction, although nitrogen mass balance was well satisfied during the reaction. Again the oxygen species remain adsorbed on the catalyst.

DISCUSSION

Reaction Mechanism for the Reduction of Nitric Oxide with Hydrogen

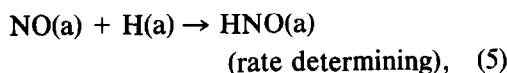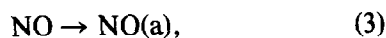The negative order (-0.9) in nitric oxide for the formation of nitrous oxide in the reduction on Co–TPP/TiO$_2$ may be explained in terms of the following schemes: (i) a strong adsorption of nitric oxide retards the adsorption of hydrogen, where both gases may be adsorbed on the same site, or nitric oxide adsorbed on the central metal ion may influence the site for hydrogen to retard the adsorption of the latter gas, (ii) a stable species like N$_2$O$_2$ is produced over the catalyst under a higher pressure of nitric oxide, and (iii) a strong adsorption of nitrous oxide derived from nitric oxide occupies the active site to retard the reaction. Although the formation of dimeric nitric oxide over chromia has been reported (7), there is no spectroscopic indication of such species over Co–TPP/TiO$_2$ at the reaction temperatures. The dimers are believed to coordinate through their oxygen atoms; however, the ir spectrum of the adsorbed nitric oxide indicates that its coordination is through the nitrogen atom to the cobalt. The last case (iii) can be ruled out because the adsorption of nitrous oxide was revealed to be much weaker than that of nitric oxide in the present study. Thus, the reaction order of -0.9 in nitric oxide was assumed to be due to its strong adsorption. The adsorption of nitric oxide was slightly but definitely suppressed by hydrogen, indicating that both adsorptions are mutually

influenced. Taking account of the order of 0.6 in hydrogen, the reaction can be assumed to proceed via a surface reaction of the Langmuir–Hinshelwood type between dissociatively adsorbed hydrogen and strongly adsorbed nitric oxide. The following rate equation is derived:

$$V_{N_2O} = \frac{kK_{NO}K_{H_2}P_{NO}P_{H_2}^{1/2}}{(1 + K_{NO}P_{NO} + K_{H_2}P_{H_2}^{1/2})^2}, \quad (2)$$

where k and K are the rate and the adsorption equilibrium constants, respectively. When the adsorption of nitric oxide is strong, this equation suggests the reaction orders of -1 and 0.5 for nitric oxide and hydrogen, respectively. Equation (2) usually assumes the same adsorption sites for nitric oxide and hydrogen. The central metal ion (partially reduced) and the porphyrin anion radical, which is induced by supporting Co–TPP on TiO$_2$ (4), can be reasonably assumed to be the sites for nitric oxide and hydrogen, respectively. Through an overlap of the $d\pi$ orbital of the central metal ion with the π^* orbital of the porphyrin ring, the adsorption of nitric oxide on the cobalt ion may decrease the anionic nature of the porphyrin ring, resulting in hindrance of hydrogen adsorption on the latter site. Equation (2) can be applicable for such a situation of the reaction where the adjacent active sites for the different species may participate.

A sequence of the following steps can be proposed:

$$NO \rightarrow NO(a), \quad (3)$$

$$\tfrac{1}{2}H_2 \rightarrow H(a), \quad (4)$$

$$NO(a) + H(a) \rightarrow HNO(a)$$
$$\text{(rate determining)}, \quad (5)$$

$$HNO(a) + NO \rightarrow N_2O + OH(a), \quad (6)$$

$$OH(a) + H(a) \rightarrow H_2O. \quad (7)$$

Adsorption steps (3) and (4) are rapid in comparison with the following step as revealed in the present study. HNO(a) may be an intermediate species for the selective

formation of nitrous oxide, leading to neither molecular nitrogen nor ammonia. Reduction of cobalt ion induced by TiO₂ as described previously (4) may activate nitric oxide.

Ayen and Peters (8), Shelef and Gandhi (9), Taylor and Klimisch (10), and Matson and Harriott (11) have discussed the reaction mechanism for the catalytic reduction of nitric oxide with hydrogen over ruthenium catalyst. The product distribution and the reaction orders over the catalyst are very similar to those on Co–TPP. In contrast, Co–TPP dispersed on SiO₂ (abbreviated Co–TPP/SiO₂, Co–TPP 5 wt%) was found recently to produce molecular nitrogen, nitrous oxide, and ammonia with positive reaction orders both in nitric oxide and hydrogen, suggesting a different reaction mechanism. Thus, an electronic interaction of Co–TPP with the supporting titanium dioxide strongly modifies the catalytic nature of Co–TPP such that it behaves like the noble metal. A partially reduced cobalt ion (described as Co$^{2-\delta}$) which is induced by accepting electrons from the support may effectively weaken the nitrogen–oxygen bond by emphasizing the anionic nature (1–4) of the adsorbed nitric oxide. In addition, adsorption and activation of hydrogen, which is derived by an electron transfer from the support to the porphyrin ring, may also be responsible for the catalytic characteristics of Co–TPP/TiO₂.

Different Reactivities and Adsorption Abilities of Nitric Oxide and Nitrous Oxide

The different reactivities of nitric oxide and nitrous oxide with hydrogen over Co–TPP/TiO₂ in their competitive reaction (Fig. 1) should be associated with their different adsorption abilities. Otto and Shelef (12) demonstrated the same trend in their reactivities on ruthenium catalyst. The adsorption of nitrous oxide has been established experimentally to be generally weaker than that of nitric oxide on various metal oxides (13, 14). The poor electron density on the terminal nitrogen atom of nitrous oxide (15), which interacts with the $d\sigma$ orbitals of metal ions, may be the reason, although reactivities in their single reactions were similar.

Decomposition of Nitric Oxide and Nitrous Oxide without Reductant

In the decomposition of nitric oxide over Co–TPP/TiO₂, nitrous oxide along with traces of molecular nitrogen was produced when neither molecular oxygen in the gas phase nor changes in the oxidation state of the central metal ion were detected. Che et al. (16) reported the formation of nitrous oxide and oxidation of palladium in the decomposition of nitric oxide over Pd⁰–Y-zeolite prereduced by hydrogen. Steinbach and Joswig (17) reported the formation of molecular nitrogen and oxygen adsorbed on Mn- and Fe-phthalocyanines in the decomposition of nitric oxide above 300°C. Thus, the decomposition probably takes place leaving oxygen species on Co–TPP. On the other hand, titanium dioxide, which is an n-type semiconductor, contains a certain amount of Ti³⁺ ions (18). Adsorption of oxygen as O₂⁻ was demonstrated on reduced or photo-irradiated titanium dioxide (19, 20). It has also been reported that nitrous oxide can interact with TiO₂ which is prereduced (21) or irradiated (22), producing O⁻ species on its surface. These facts suggest that TiO₂ can provide the adsorption site for the residual oxygen derived from the decomposition of nitric oxide and nitrous oxide, even though the reaction itself occurs on Co–TPP. Such an oxygen transfer may be called a kind of spillover phenomenon. Thus, the turnover number of the decomposition (mole ratio of NO reacted/Co ion) can be up to 12. The decomposition of nitric oxide without any reductant is most preferable for the removal of pollutant nitric oxide.

The details of the reaction, including the catalyst life, are now being studied.

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