

The kinetic study for reduction of NO by CO over cobalt tetraphenylporphyrin supported on titanium dioxide*

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Abstract—The catalytic reduction of nitric oxide by carbon monoxide over cobalt tetraphenylporphyrin supported on titanium dioxide (Co-TPP/TiO₂) has been investigated. Co-TPP/TiO₂ pretreated by evacuation at 270°C exhibited a remarkable activity. The kinetic equation for the reduction of nitric oxide by carbon monoxide in the reaction temperature ranging from 80 to 150°C ($v=kP_{\text{NO}}^{0.56}P_{\text{CO}}^{0.41}$) suggested that the reaction can be assumed to occur via a surface reaction of the Langmuir-Hinshelwood model between nitric oxide and carbon monoxide adsorbed on the central metal ion of Co-TPP. Experimental results indicated that the reduction of nitric oxide and formation of molecular nitrogen took place simultaneously during initial stage of the reaction. The apparent activation energy was calculated to be 30.8 kJ/mol.

Keywords: catalytic reduction; nitric oxide; kinetic study.

INTRODUCTION

Since nitric oxide was recognized as one of the environmental pollutant gases to be removed, the catalytic reduction of nitric oxide with various reducing agents has been intensively investigated, using noble metal or metal oxide and perovskite catalysts. The catalytic activity of transition metal macrocyclic complexes supported on titania for the reduction of nitric oxide by carbon monoxide and its kinetic study have been seldom reported. Metal porphyrin molecules square planer complexes can offer their axial sites to coordinate with nitric oxide and carbon monoxide and enhanced their reaction activities. Co-TPP supported on TiO₂ pretreated by the evacuation at 270°C exhibited a remarkable activity for the reduction of nitric oxide by carbon monoxide around 100°C. Such a significant enhancement of catalytic activity of Co-TPP supported on TiO₂ may be explained in terms of the electron transfer from the support to the complex and increase of the effective surface area of Co-TPP. In the present paper the catalytic

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activity for the reduction of nitric oxide by carbon monoxide over Co-TPP/TiO₂ was investigated. The kinetic study of the reduction was performed with respect to reaction orders and apparent activation energy. The reaction can be assumed to proceed via a surface reaction of Langmuir-Hinshelwood type between nitric oxide and carbon monoxide adsorbed on the central metal ion of Co-TPP.

EXPERIMENTAL METHODS

Materials

H₂TPP was synthesized according to the method of Alder (Alder, 1967). The purity of the compound was examined by elemental analysis and UV spectroscopy (Shimazu UV-3000) calcd.: C 85.90%, H 4.92%, N 9.12%; obsd.: C 85.86%, H 4.89%, N 9.06%; λ_{max} ($\epsilon \times 10^{-3}$): 414nm, 514nm, 550nm, 590nm and 647nm.

Co-TPP was synthesized by the reaction of H₂TPP and Co (CH₃COO)₂ · 4H₂O in D. M. F. solution. The purity of the complex was examined by elemental analysis and UV spectroscopy calcd.: C 78.69%, H 4.20%, N 8.34%; obsd.: C 78.52%, H 4.25%, N 8.20%; Q band 528nm; Soret band 413nm

TiO₂ was prepared by precipitation from titanium sulphate and calcined in air at 110°C, 10hr. 20-40 mesh. The BET surface area was 251 m²/g.

Co-TPP/TiO₂: TiO₂ was added to a red-purple solution of Co-TPP in benzene and kept at room temperature for 24hr, removing the solvent under reduced pressure, a green slurry of Co-TPP/TiO₂ (5wt % Co-TPP) was prepared.

NO was prepared by the reaction of NaNO₂ and FeSO₄ (The N₂ impurity could not be removed, but was accounted for determining the rate of nitrogen produced during nitric oxide reduction). CO was obtained from Beijing Analytical Instrumental Factory. All gases were purified prior to use. Helium (99.999%) was used as dilute gas.

Procedure

All catalytic reaction were performed in a closed-circulation reactor (volume: 1200ml) with a fixed catalyst bed, the circulating rate was 300-500ml/min. which was attained with a magnetically driven piston. The amount of catalyst was 2-4g. The products (N₂O and N₂) and the reactants (NO and CO) were analyzed by a gas chromatograph using column packed with 5A molecular sieve (4mm i.d., 2m long). Partial pressure of nitric oxide and carbon monoxide were regulated in the range of 6.7-65.5 torr and 34.8-96.1 torr, respectively for the kinetic study at the temperature ranging from 80-150°C. The conversion and yields were reproduced with $\pm 5\%$ error.

The adsorption of nitric oxide and nitrous oxide were observed volumetrically with a glass apparatus equipped with a digital barometer (Model 361, setra systems, INC. U. S. A.) connected to a vacuum line and a gas reservoirs. After the adsorbent (3g) was evacuated at the fixed temperature for 1hr, the nitric oxide (or nitrous oxide) was introduced so that it was in

contact with the adsorbent, its uptake being monitored by means of a digital barometer.

RESULTS AND DISCUSSION

Catalytic activity of Co-TPP/TiO₂ for the reduction of NO with CO

The catalytic reaction was carried out at variable temperature from 80–150°C using 4g Co-TPP/TiO₂ pretreated by evacuation (1×10^{-2} torr) at 250–270°C for 1hr, partial pressures of each component were $P_{NO} = 21$ torr, $P_{CO} = 48$ torr, $P_{N_2} = 6$ torr (impurity) and $P_{H_2} = 605$ torr.

The reduction of nitric oxide with formation of nitrous oxide and molecular nitrogen changes with time were shown in Figure 1. Where the reaction temperature was 100°C. It took 48 min and 155 min to complete the conversion of nitric oxide and nitrous oxide, respectively.

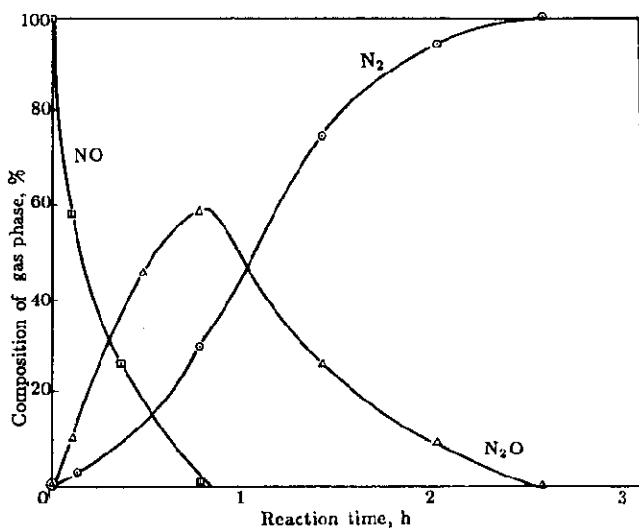


Fig. 1 The curve of NO reduction with CO over Co-TPP/TiO₂
Cat.: 4g (evacuated at 270°C 1hr) Reaction temp.: 100°C.

Experimental results indicated that the reduction of nitric oxide and formation of molecular nitrogen took place simultaneously during initial stage of the reaction unlike the reduction of nitric oxide with hydrogen (Isao, 1982), nitrous oxide was the only nitrogen-containing product at the early stage of the reaction. Nitrogen was produced just only after nitric oxide was consumed completely in the gas phase. The reaction time for the reduction of nitric oxide and nitrous oxide at different temperature are shown in Table 1. As the temperature increased from 100 to 200°C, the reaction time reduced to one-fourth of the time during which nitric oxide was converted into nitrogen completely at 100°C. The effects of temperature on the reduction rate of nitric oxide by carbon monoxide are shown in Table 2. As the temperature increases from 50 to 150°C the catalytic activity of Co-TPP/TiO₂ increases from 0.52 to 2.8m mole/g-cat. hr.

The activity of the catalyst definitely decreased in the second run. However the evacuation (1×10^{-2} torr) of the same catalyst at 150°C for 0.5 hr before using the initial activity was restored.

Table 1 Reaction time (min) for the reduction of NO and N_2O

Type of reaction	Reaction temperature, $^\circ\text{C}$			
	80	100	150	200
$\text{NO} \rightarrow \text{N}_2\text{O}, \text{N}_2$	96	58		
$\text{N}_2\text{O} \rightarrow \text{N}_2$	196*	198	80	50

Cat.: 4g (evacuated at 250°C 1hr.)

Initial pressure: $P_{\text{NO}} = 21$ torr, $P_{\text{CO}} = 48$ torr, $P_{\text{N}_2} = 6$ torr,
 $P_{\text{H}_2} = 603$ torr.

* The conversion of N_2O is 60% at 196min.

Table 2 Effect of temperature on the rate for reduction of NO by CO over Co-TPF/ TiO_2

Reaction temp., $^\circ\text{C}$	Initial pressure, torr		Conversion rate of NO*, mmole /g-cat. hr.
	P_{NO}	P_{CO}	
	50	52	77
100	66	76	0.78
125	55	71	2.20
150	54	73	2.80

Cat.: 4g (evacuated at 270°C 1hr.)

* The rates are the average value during 10 minute

No reaction was observed on unsupported Co-TPP at 100°C under the same condition indicating that supporting Co-TPP on TiO_2 remarkable enhanced its catalytic activity for the reduction of nitric oxide by carbon monoxide. The enhancement may be related to the electron

transfer from the support to the complex. The strong interaction of Co-TPP and TiO₂ took place.

Adsorption measurements of nitric oxide and nitrous oxide

The amounts of adsorbed nitric oxide or nitrous oxide over Co-TPP/TiO₂ during the reaction of nitric oxide (without carbon monoxide) in the circulating reactor were observed. The results are listed in Table 3. The effect of adsorption of nitric oxide on the calculated rate values in this work is negligible. The adsorption level 20 min after the introduction of NO or N₂O no significant decomposition took place.

Table 3 Adsorption of NO and N₂O over Co-TPP/TiO₂

Reaction temp., °C	Adsorbed NO, μ mol/g-cat.	Adsorbed N ₂ O, μ mol/g-cat
100	39.2	16.9

Cat.: 3g, P_{NO} = 75 torr, P_{N₂O} = 36 torr.

Kinetic study of NO reduction with CO over Co-Tpp/TiO₂

The rates of reduction of nitric oxide with carbon monoxide using 2g Co-TPP/TiO₂ at the temperature ranging from 80 to 150°C and the pressure of nitric oxide and carbon monoxide varying from 6.7–65.5 torr and 34.8–96.1 torr, respectively were observed. On the basis of these results, the rates V for the conversion of nitric oxide are calculated by the equation

$$V = \frac{(x/100) \cdot (1000 \cdot P_{\text{NO}} \cdot V/RT)}{t \cdot w} \text{ (mmole/g-cat.hr)}$$

x : conversion of NO or yield of N₂O or N₂ (%)

P_{NO} : initial pressure of NO

V : volume of reactor

t : reaction time

w : catalyst weight

The rates are calculated on the base of the average values of the conversion of NO between 15 to 25 min. The data from each runs are fit to power-law expression of the form

$$V = k P_{\text{NO}}^m P_{\text{CO}}^n \quad (1)$$

where k is the rate coefficient, m and n are the reaction orders with respect to NO and CO,

respectively. Since $k = Ae^{-E_a/RT}$ obtained, then

$$V = Ae^{-E_a/RT} P_{\text{NO}}^m P_{\text{CO}}^n \quad (2)$$

Regression calculation was used to determine the values of A , E_a , m and n in equation (2). The results show that $m = 0.56$, $n = 0.41$, $E_a = 30.8$ kJ/mol and $A = 236$.

Taking account of the order of 0.56 for nitric oxide and 0.41 for carbon monoxide respectively, both of them are close to 0.5, the reaction can be assumed to proceed via a surface reaction of the Langmuir-Hinshelwood process between nitric oxide and carbon monoxide adsorbed on the active sites. The following rate equation is derived

$$V = \frac{K a_{\text{NO}} a_{\text{CO}} P_{\text{NO}} P_{\text{CO}}}{(1 + a_{\text{NO}} P_{\text{NO}} + a_{\text{CO}} P_{\text{CO}} + \dots)^2} \quad (3)$$

where K represents the rate coefficient and a_{NO} , a_{CO} represent the adsorption equilibrium constants. It is assumed that the reaction is limited by adsorbed nitric oxide and carbon monoxide, the others are very weakly adsorbed. Equation (3) can be simplified into equation (4)

$$V = \frac{K a_{\text{NO}} a_{\text{CO}} P_{\text{NO}} P_{\text{CO}}}{(1 + a_{\text{NO}} P_{\text{NO}} + a_{\text{CO}} P_{\text{CO}})^2} \quad (4)$$

if

$$a = (K a_{\text{NO}} a_{\text{CO}})^{-1/2}$$

$$b = (K^{-1} a_{\text{NO}} a_{\text{CO}}^{-1})^{1/2}$$

$$c = (K^{-1} a_{\text{CO}} a_{\text{NO}}^{-1})^{1/2}$$

Eq. (4) can be expressed as

$$\left(\frac{P_{\text{NO}} P_{\text{CO}}}{V}\right)^{1/2} = a + b P_{\text{NO}} + c P_{\text{CO}} \quad (5)$$

The regression calculation is performed to evaluate the values of a , b , c in equation (5). Data of P_{NO} , P_{CO} and V at the temperature of 80, 125, 150 °C are used in this regression calculation. Results are listed in Table 4. The correlation coefficients (r) at different temperature are larger than 0.99 which suggests that the rate data are fit to equation (4).

Table 4 Results of regression calculation for partial pressure and rates by Equation (5)

Reaction temp., °C	a	b	c	r	a_{NO}	a_{CO}	K	Number of data points
80	68.6345	0.2413	0.1143	0.9972	3.5×10^{-3}	1.7×10^{-3}	36.2582	7
125	24.4170	0.3036	0.1219	0.9991	1.2×10^{-2}	0.5×10^{-2}	27.0270	7
150	9.6849	0.4484	0.2557	0.9986	4.6×10^{-2}	2.6×10^{-2}	8.7222	8

The following steps can be proposed (rate determining)

1. $\text{NO} \rightleftharpoons \text{NO}_{(a)}$
2. $\text{CO} \rightleftharpoons \text{CO}_{(a)}$
3. $\text{NO}_{(a)} + \text{CO}_{(a)} \longrightarrow \text{N}_{(a)} + \text{CO}_{2(a)}$ (rate determining)
4. $\text{NO}_{(a)} + \text{N}_{(a)} \longrightarrow \text{N}_2\text{O}$
5. $\text{NO}_{(a)} + \text{N}_{(a)} \longrightarrow \text{N}_2 + \text{O}_{(a)}$
6. $\text{N}_2\text{O} \rightleftharpoons \text{N}_2\text{O}_{(a)}$
7. $\text{N}_2\text{O}_{(a)} + \text{CO}_{(a)} \longrightarrow \text{N}_2 + \text{CO}_2$
8. $\text{CO}_{(a)} + \text{O}_{(a)} \longrightarrow \text{CO}_2$

Based on the experimental results it is desirable to introduce several assumptions. The first is that the adsorption and desorption rates of nitric oxide and carbon monoxide are much more rapid than the reduction rate of nitric oxide and hence, that the surface is dominated by both reactants (NO and CO) represented by equation (4). The second assumption is that reaction 3 is the rate-limiting step in the mechanism. The third is the competitive adsorption of nitrous oxide is weaker than that of nitric oxide, or carbon monoxide adsorbed on the central metal ion may influence and favour the adsorption of nitrous oxide, or we may say that the activation of carbon monoxide on the active site may be favour to enhance the catalytic activity. Further detail study on the catalytic activity of metal macrocyclic complexes are now in progress.

REFERENCES

- Adler, A. D. *et al.*, J. Org. Chem., 1967, 32:476
Isao Mochida, *et al.*, J. Catal., 1982, 77: 519