

REMARKABLE CATALYTIC ACTIVITY OF THERMALLY MODIFIED CoTPP  
SUPPORTED ON  $\text{TiO}_2$  FOR NO-CO REACTION

Isao MOCHIDA,<sup>\*</sup> Yasuo IWAI,<sup>+</sup> and Hiroshi FUJITSU

Research Institute of Industrial Science,  
Kyushu University, Kasuga 816

<sup>+</sup>Department of Molecular Technology,  
Graduate School of Industrial Sciences,  
Kyushu University, Kasuga 816

CoTPP supported on fine  $\text{TiO}_2$ -120s pretreated by the evacuation at 250 °C exhibited a remarkable activity, 2.2 mol NO/mol Co·min, for the reduction of NO with CO at 100 °C. The pretreatment modified the structures of CoTPP to be insoluble in benzene but still soluble in quinoline. Such an activity is assumed to originate from the thermally-modified CoTPP of dimeric form with major loss of phenyl groups interacting more favorably with the properly dehydrated support.

It may be one of the most fruitful approaches for the design of novel catalysts or sensors to utilize properly the favorable catalytic species-support interaction. The present authors have reported that supporting Co-tetraphenylporphyrin (CoTPP) on a titania from titanyl sulfate calcined at 300 °C ( $\text{TiO}_2$ -300, 165 m<sup>2</sup>/g) causes a marked electron transfer, forming  $\text{Co}^{2-\delta}\text{TPP}^{\bar{\nu}}$  to exhibit a significant catalytic activity for the reduction of NO at 100 °C<sup>1-4)</sup> and the oxidation of CO at 17 °C.<sup>5)</sup> Its maximum activity of 6.3x10<sup>-1</sup> mol NO/mol Co·min was obtained when the catalyst is evacuated at 200 °C.

In the present study, a series of heat-treatment of CoTPP supported on titania ( $\text{TiO}_2$ -120s) which had large surface area (240 m<sup>2</sup>/g) in spite of the same source was examined to find higher catalytic activity for the reduction of NO, since the modification of the ligand structure may strongly influence the activity. The ligand structure of the complex has been reported to be

thermally modified at rather high temperatures (300–600 °C) to exhibit a better catalytic activity for the electrochemical reduction of oxygen when it was supported on active carbon.<sup>6)</sup>

Co-TPP was synthesized by Adlers' method.<sup>7)</sup> TiO<sub>2</sub>-120s, which was prepared by precipitation from titanyl sulfate with seeds followed by calcination at 120°C (240 m<sup>2</sup>/g, 8.1wt% SO<sub>4</sub>), was provided by Titan Kogyo Co. CoTPP was impregnated on TiO<sub>2</sub>-120s using a benzene solution (supported CoTPP:5wt%). CoTPP/TiO<sub>2</sub>-120s thus prepared, was evacuated (2X10<sup>-3</sup> Torr) at variable temperatures before the reaction. The catalytic reaction was carried out at 100 °C, using a circulating reactor (vol. 800 ml, circulation rate 500 ml/min). Catalyst amount and partial pressures of NO and CO were 4 g, 10 and 20 cmHg, respectively

CoTPP/TiO<sub>2</sub>-120s exhibited a significant catalytic activity for NO-CO reaction at 100 °C which depended markedly on evacuation conditions (Fig.1). Below 200 °C of the evacuation temperature, its activity was rather low even if long evacuation time and/or high vacuum were applied. Evacuation at 200°C for 18h increased the activity of CoTPP/TiO<sub>2</sub>-120s to reach 9.7X10<sup>-1</sup> mol NO/mol NO/mol Co·min. The maximum activity of the catalyst was obtained by 250 °C-2 h evacuation to achieve the rate of 2.2 mol NO/mol Co·min, being ca.4 times larger than that over CoTPP/ TiO<sub>2</sub>-300, which was obtained by the evacuation at 200 °C. Further increase of the evacuation time at this temperature did not change the activity. The evacuation at 275 °C, however, caused a significant decrease of activity. Such a high activity is four thousand times that of unsupported CoTPP for the same reaction. Supporting CoTPP on the TiO<sub>2</sub>-120s which was evacuated at 250 °C before the impregnation gave a much inferior activity (9.6X10<sup>-2</sup> mol NO/mol Co·min) after the evacuation at the reaction temperature. These results suggest favorable manifestation of catalyst-support interactions with the

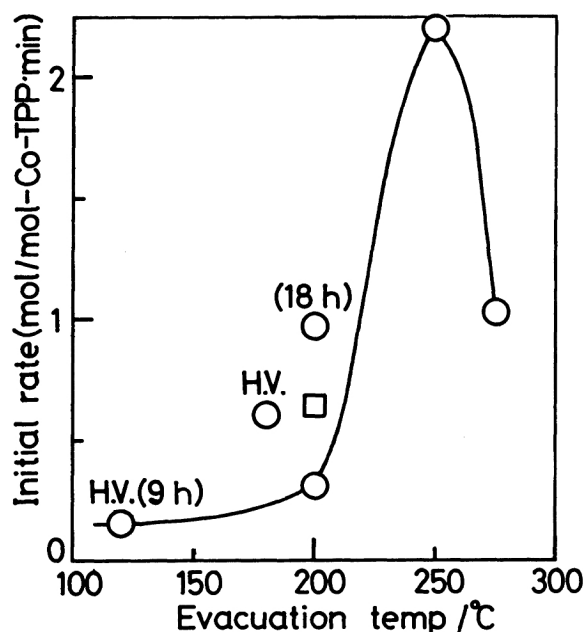


Fig.1. Effects of evacuation temperature on the catalytic activity of CoTPP/TiO<sub>2</sub>-120s for NO-CO reaction.

Cat.:4 g, NO:10 cmHg, CO:20 cmHg,  
 react. temp.:100 °C,  
 evacuation time:2 h,  
 □ :TiO<sub>2</sub>-300, 200 °C-1 h evacuated,  
 H.V.:1 X 10<sup>-5</sup> Torr.

modified complex.

The reaction profile of NO-CO reaction at 100 °C over CoTPP/TiO<sub>2</sub>-120s evacuated at 250 °C for 2 h is illustrated in Fig. 2, where the activity of CoTPP supported on TiO<sub>2</sub>-120s compared with that on TiO<sub>2</sub>-300, is remarkable. The reaction seems to proceed on both catalysts in a consecutive manner of NO→N<sub>2</sub>O→N<sub>2</sub>.

In contrast, the reduction rate of NO with H<sub>2</sub> (NO:10 cmHg, H<sub>2</sub>:20 cmHg) on CoTPP/TiO<sub>2</sub>-120s was much smaller than that with CO by one fortieth. Such a rate is a half of that on CoTPP/TiO<sub>2</sub>-300. However, higher pressure of H<sub>2</sub> (H<sub>2</sub>:60 cmHg, NO:2 cmHg) gave the same rates on both catalysts.

Although adsorption of NO and CO could not be measured during the reaction because of the too fast reaction on CoTPP/TiO<sub>2</sub>-120s evacuated at 250 °C-2 h, 5.8 and 3.8 ml(STP)/g<sub>cat</sub> of their respective adsorption were observed at room temperature. Such amounts were a half for NO and ca. 1.5 times larger for CO compared to those on CoTPP/TiO<sub>2</sub>-300. These results suggest that the activation of CO on the present catalyst may be the principal reason for such a remarkably high activity.

The evacuation at 250 °C for 2 h modified CoTPP on TiO<sub>2</sub>-120s in terms of its colour from dull green to brown and its solubility in benzene (78% became unextractable), whereas CoTPP on TiO<sub>2</sub>-300 was completely extractable with benzene without any structural change.<sup>4)</sup> The same activity was maintained after the extraction with benzene, however quinoline extraction (99% of the complex extractable) lost the catalytic activity. The structure of quinoline soluble-benzene insoluble complex appeared to be very much modified based on the averaged molecular weight ( $\overline{MW}$ :660, containing ca. 2 Co), and IR (considerable decrease of the peaks due to phenyl group), some oligomerization with major removal of phenyl groups being suggested as reported for the

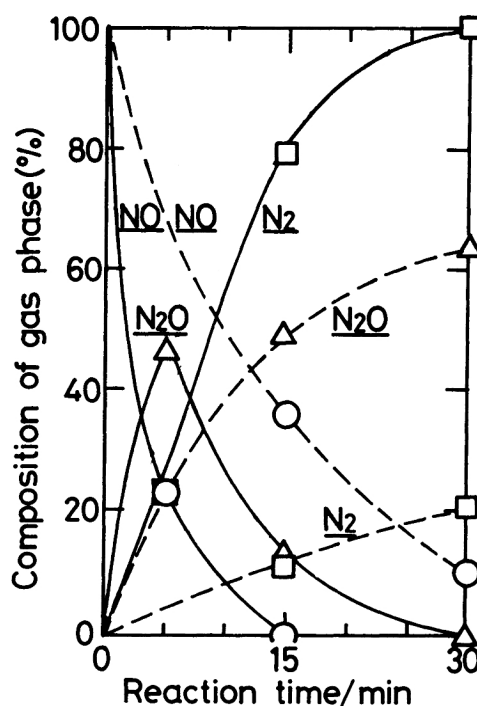


Fig.2. Reduction profile of NO with CO over CoTPP/TiO<sub>2</sub>-120s at 100 °C. Cat.:4 g, NO:10 cmHg, CO:20 cmHg, evacuation:250 °C-2 h, —:CoTPP/TiO<sub>2</sub>-120s, ---:CoTPP/TiO<sub>2</sub>-300. (evacuated at 200 °C-2 h)

heat-treatment of CoTPP on active carbon.<sup>6)</sup> Such structural modification of the complex by the evacuation at a particular temperature of 250 °C allows more favorable interaction between the complex and the support which may cause the extraordinary activity. The modified structure of CoTPP may accept the electrons at the central metal ion more easily to be most favorable for the activation of CO, missing the activation ability for hydrogen because of the significant change of ligand structure.

The support may be also favorably activated by the heat-treatment as observed previously.<sup>4)</sup> More hydroxyl groups on the amorphous structure of original TiO<sub>2</sub>-l20s are most properly dehydrated at 250 °C under vacuum to provide most active sites for electron-donation to the supported CoTPP.

Such an interaction between the complex of the best structure and the support properly prepared may be one of the most important factors to be taken into account when better catalysts as well as sensors are designed. Further detail study on the structure of the modified complex is now in progress.

#### References

- 1) I. Mochida, K. Tsuji, K. Suetsugu, H. Fujitsu, and K. Takeshita, J. Phys. Chem., 84, 3159 (1980)
- 2) I. Mochida, K. Suetsugu, H. Fujitsu, K. Takeshita, K. Tsuji, Y. Sagara, and A. Ohyoshi, J. Catal., 77, 519 (1982)
- 3) I. Mochida, K. Suetsugu, H. Fujitsu, and K. Takeshita, J. Chem. Soc., Chem. Commun., 1982, 166
- 4) I. Mochida, K. Suetsugu, H. Fujitsu, and K. Takeshita, J. Phys. Chem., 87, 1524 (1983)
- 5) I. Mochida, K. Suetsugu, H. Fujitsu, and K. Takeshita, Chem. Lett., 1983, 177
- 6) J. A. Rob von Veen, J. F. van Baar, and K. J. Kroese, J. Chem. Soc., Faraday Trans. 1, 77, 2827 (1981)
- 7) A. D. Adler, F. L. Longo, F. Kampas, and J. Kim, J. Inorg. Nucl. Chem., 32, 2443 (1970)

(Received November 7, 1983)