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REMARKABLE CATALYTIC ACTIVITY OF THERMALLY MODIFIED CoTPP SUPPORTED ON TiO_2 FOR NO-CO REACTION

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CoTPP supported on fine 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 (TiO_2-300, 165 m^2/g) causes a marked electron transfer, forming $Co^{2-\delta}TPP^{\bar{\bullet}}$ to exhibit a significant catalytic activity for the reductin of NO at 100 °C[1-4] and the oxidation of CO at 17 °C.[5] Its maximum activity of 6.3×10^{-1} 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 (TiO_2-120s) which had large surface area (240 m^2/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.6)

Co-TPP was synthesized by Adlers' method.7) TiO_2-120s, which was prepared by precipitation from titanyl sulfate with seeds followed by calcination at 120°C (240 m^2/g, 8.1wt% SO_4), was provided by Titan Kogyo Co. CoTPP was impregnated on TiO_2-120s using a benzene solution (supported CoTPP:5wt%). CoTPP/TiO_2-120s thus prepared, was evacuated ($2X10^{-3}$ 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_2-120s 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_2-120s to reach $9.7X10^{-1}$ 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_2-300, 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_2-120s which was evacuated at 250 °C before the impregnation gave a much inferior activity ($9.6X10^{-2}$ mol NO/mol Co•min) after the evacuation at the reaction temperature. These results suggest favorable manifestation of catalyst-support interactions with the

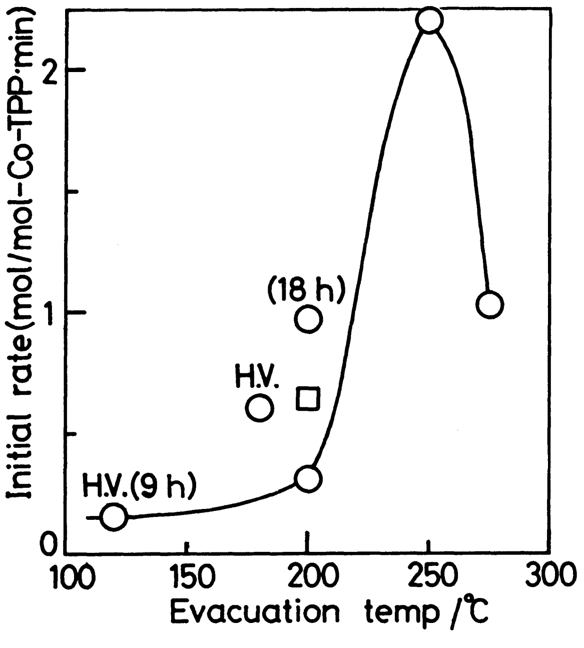

Fig.1. Effects of evacuation temperature on the catalytic activity of CoTPP/TiO_2-120s for NO-CO reaction.
Cat.:4 g, NO:10 cmHg, CO:20 cmHg, react. temp.:100 °C, evacuation time:2 h,
□ :TiO_2-300, 200 °C-1 h evacuated,
H.V.:$1 X 10^{-5}$ Torr.

modified complex.

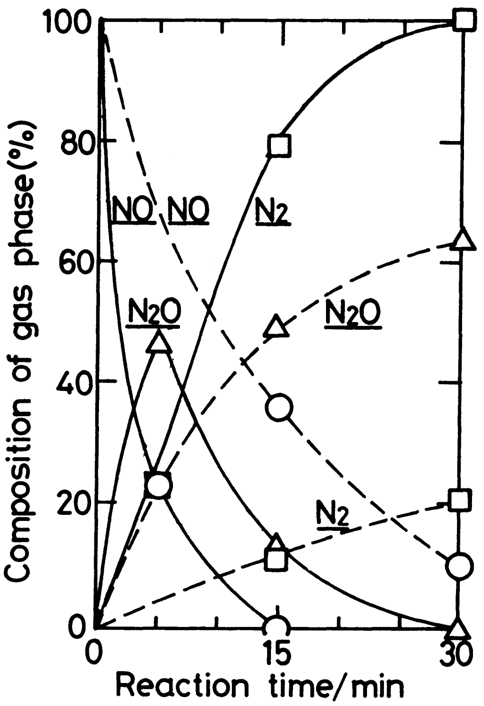

Fig.2. Reduction profile of NO with CO over $CoTPP/TiO_2$-120s at 100 °C. Cat.:4 g, NO:10 cmHg, CO:20 cmHg, evacuation:250 °C-2 h, ———:$CoTPP/TiO_2$-120s, – – – –:$CoTPP/TiO_2$-300. (evacuated at 200 °C-2 h)

The reaction profile of NO-CO reaction at 100 °C over $CoTPP/TiO_2$-120s evacuated at 250 °C for 2 h is illustrated in Fig. 2, where the activity of CoTPP supported on TiO_2-120s compared with that on TiO_2-300, is remarkable. The reaction seems to proceed on both catalysts in a consecutive manner of $NO \rightarrow N_2O \rightarrow N_2$.

In contrast, the reduction rate of NO with H_2 (NO:10 cmHg, H_2:20 cmHg) on $CoTPP/TiO_2$-120s was much smaller than that with CO by one fortieth. Such a rate is a half of that on $CoTPP/TiO_2$-300. However, higher pressure of H_2 (H_2:60 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 $CoTPP/TiO_2$-120s evacuated at 250 °C-2 h, 5.8 and 3.8 ml(STP)/g_{cat} 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 $CoTPP/TiO_2$-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_2-120s in terms of its colour from dull green to brown and its solubility in benzene (78% became unextractable), whereas CoTPP on TiO_2-300 was completely extractable with benzene without any structural change.$^{4)}$ 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, containting 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 heat-treatment of CoTPP on active carbon.$^{6)}$ Such structural modification of the complex by the evacuation at a paticular 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 favarable for the activation of CO, missing the activation ability for hydrogen because of the significant change of ligand structure.

The support may be also favarably activated by the heat-treatment as observed previously.$^{4)}$ More hydroxyl groups on the amorphous structure of original TiO_2-120s 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.

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