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Catalytic Activity for NO Decomposition of Cobalt Tetrapropoxyphthalocyanine Supported on Titania

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Cobalt-tetrapropoxyphthalocyanine, CoPc(OPr)$_4$, impregnated with THF onto TiO_2 provided an anion radical (g value:2.003) which gave a stationary NO(500 ppm) conversion of 27% in a flow reaction without oxygen at 423 K. Oxygen in the reactant gas increased the conversion to 55%, which decreased gradually to the stationary 27% without any formation of NO_2 or CO_2.

Although selective reduction of NOx with ammonia into N_2 and H_2O has been applied practically in various industries of advanced countries,$^{1)}$ its decomposition into N_2 and O_2 would be very desirable as an energy-saving process for mobile sources, where ammonia is difficult to store.$^{2)}$ There are several proposals to decompose NO on noble metals,$^{3)}$ copper ion-exchanged zeolite$^{4)}$ and some oxides.$^{5)}$ High temperature for sufficient catalytic activity$^{6)}$ or oxygen inhibition$^{7)}$ restricts their application.

The present authors reported that the catalytic activity of cobalt tetraphenylporphyrin(CoTPP) supported on TiO_2 was active for this reaction at a lower temperature around 373 K.$^{8)}$ Supposedly this activity originated from the strong electronic interaction between the complex and the support. However, its combustion in the presence of oxygen inhibited its practical application.$^{8)}$ Co-phthalocyanine(Co-Pc) of low solubility is more stable than CoTPP at temperatures up to 473 K even in air. Since the unsupported complex exhibited catalytic activity for NO reduction as neat CoTPP,$^{9)}$ its interaction with titania was expected to increase its activity for decomposition. Substitution on the ligand ring increases its solubility, which assures its high dispersion for the strong interaction.

CoPc(OPr)$_4$ was prepared from $CoCl_2$ and 3-propoxybenzimid, which was synthesized from 4-nitrophthalonitrile through 4-propoxyphthalonitrile. CoPc(OPr)$_4$ was impregnated onto TiO_2 (Titan Kogyo) from its benzene or THF solution (5 wt%), giving the catalysts <u>1</u> and <u>2</u> , respectively. Catalytic activities for decomposition of NO were measured by using a flow reactor after heat-treatment at 473 K for 1 h in He flow. Reaction gas consisted of 500 ppm of NO, 0 or 5% of O_2 in He. Reaction temperature and contact time (W/F) were 423 K and 3.3×10^{-2} g min ml^{-1}, respectively. NO and NO_2 were measured by a NOx meter (Yanako ECL-700) with NOx convertor. N_2O was included in NO. CO and CO_2 were analyzed by FID-GC after their conversion into CH_4. ESR spectra of the catalysts were measured at room temperature.

The catalytic activities of catalysts 1 and 2 are illustrated in Fig. 1, where the reaction was performed without oxygen for an initial period and then with 5% oxygen after 10 and 30 h for catalysts 1 and 2, respectively. Catalyst 1 showed an initial conversion of 10% without O_2, which gradually decreased to a stationary one of 6% after 10 h. Catalyst 2 showed much higher conversion (57%), which also gradually decreased within 10 h to 27%, where the conversion remained unchanged for another 20 h. The high and stable activity is remarkable. No NO_2 was detected in the product, ruling out the disproportionation of NO.

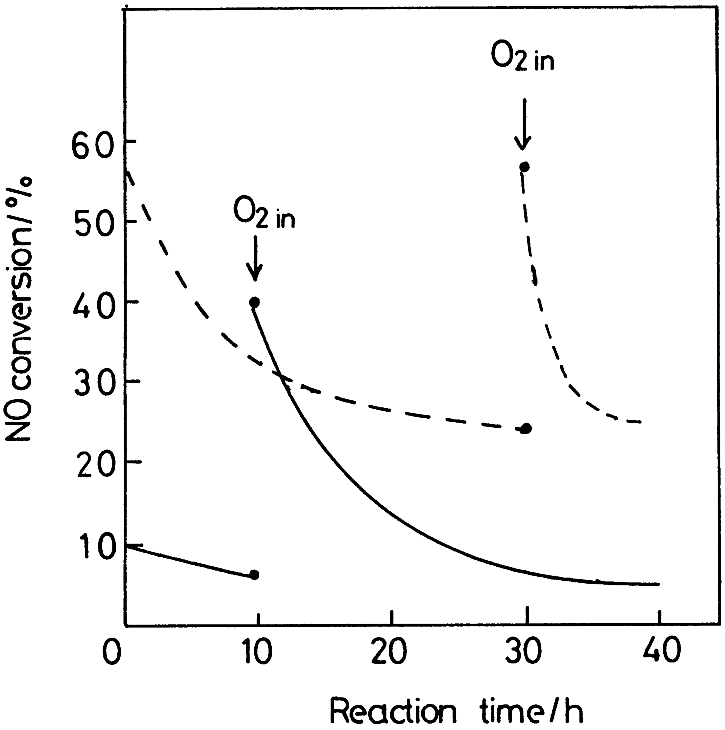

Fig. 1. Profiles of NO decomposition reaction over the catalysts 1 and 2.
Temp : 423 K, W/F=3.3×10^{-2}g min ml^{-1}
NO=500 ppm, O_2=0 or 5%, He balance
——: catalyst 1, ------: catalyst 2

Addition of oxygen (5%) into the reactant gas enhanced significantly the conversions on both catalysts temporarily as shown in Fig.1. The conversions over catalysts 1 and 2 reached to 40 and 55%, respectively. However, they decreased gradually to 6 and 27% of stationary values, respectively. Although CO_2 in comparable amounts to those of the produced N_2 was found in the product while the activity decreased, no significant amount of CO_2 and NO_2 was detected after the stationary conversion was obtained.

Figure 2 shows the adsorption isotherms of the catalysts at room temperature. The catalysts adsorbed NO almost reversibly, CO completely reversibly and O_2 irreversibly at room temperature. NO exhibited the

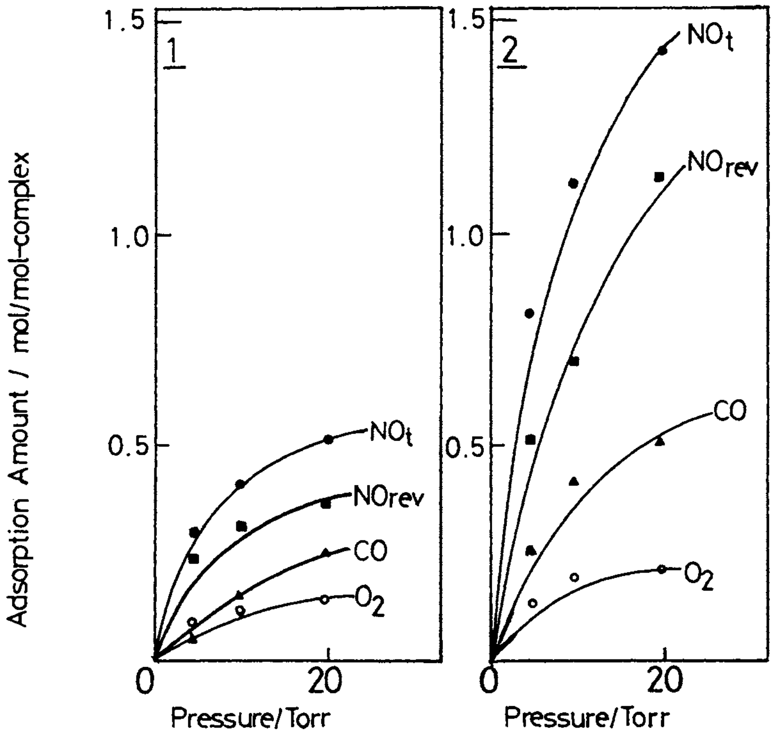

Fig. 2. Adsorption isotherm of NO, CO,and O_2 on catalysts 1 and 2. Temperature: 303 K, NO_t: total adsorbed NO, NO_{rev}: reversible portion of adsorbed NO

largest adsorption amount on both catalysts, indicating particular affinity of the complex to the substrate. Catalysts 1 and 2 adsorbed NO at the molar ratios of NO/Pc of 0.4 and 1.1 reversibly, and 0.1 and 0.3 irreversibly, respectively. Thus, catalyst 2 adsorbed about three times more NO than catalyst 1 . More adsorption of NO was also observed on catalyst 2 at 423 K, although the correct amount was difficult to count because of rapid reactions. Very small amount of adsorption was observed on TiO_2 alone.

The catalysts exhibited an ESR signal at g value of 2.003. The intensity of the signals on the catalysts 1 and 2 was 1 to 3. Introduction of NO reduced the intensity of ESR signal as previously observed.[8)]

The color and ESR signal of the catalyst suggest the electron transfer from TiO_2 to $CoPc(oPr)_4$ which produces the anion radical of the complex.[10)] The central cobalt ion in the anion radical is expected to adsorb and reduce

NO to NO^-, of which N-O bond is loosened.[11] The adsorbed NO/CoPc(OPr)$_4$ mole ratio reaches 1.4 on the catalyst 2 , suggesting the bimolecular reaction of adsorbed NO on the same complex. Oxygen produced may be transferred and stay on TiO_2, occupying the vacant site in TiO_2 as discussed on CoTPP/TiO_2 at 373 K.[8] However, its significant portion may evolve thermally at 423 K according to its decomposition pressure to determine the stationary activity.

Higher activity of catalyst(2), which was prepared by the impregnation from THF solution, appears to reflect higher dispersion of the complex on TiO_2 because of better dissolution of the CoPc(OPr)$_4$ as indicated by more adsorption abilities and stronger ESR intensity.

So far roles of added O_2 in the reactant gas are not studied in detail. Substituent groups may be oxidatively activated to reduce NO, producing CO_2. After their combustion, Pc free from OPr groups may be stable in the presence of oxygen, and can keep a similar catalytic activity to that before their oxidation, because the electronic interaction is expected to take place in the Pc skeleton. Further study to solve the origin of the catalytic activity and to find much higher catalytic activity is now under progress for practical application of the catalyst.

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