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CATALYTIC ACTIVITIES OF SOLID PORPHYRINS FOR THE REDUCTION OF NITRIC OXIDE

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Some metal-tetraphenylporphines(M-TPP) reduce NO catalytically with molecular hydrogen at elevated temperatures. The main products are N_2 and NH_3 over Co-TPP, and NH_3 over Cu-TPP, regardless of the reaction temperatures. Supporting of the complexes on silica-alumina increased the catalytic activity by a factor of eighteen.

Currently, there is great interest in studying porphirinato complexes as the model compounds of myoglobin and hemoglobin, which can carry molecular oxygen.[1) The bonding between metal ion and oxygen can activate the molecular oxygen to react with reductants in some cases of oxygen carriers. The oxidative dehydrogenation was reported to be catalyzed by cobalt-tetraphenylporphine.[2) Because the electronic structure of nitric oxide is similar to that of molecular oxygen, certain kinds of oxygen carriers can be excellent catalysts for the reduction of nitric oxide, of which removal from the atmosphere is one of the important problems to be solved urgently. Such a way of thinking may be one of the explorative approaches for the better catalysts. Sakai et al.[3) reported the catalytic activities of Schiff's bases, using sodium borohydride as the reductant. The present authors reported the catalytic activities of metal-phthalocyanines for the reduction of nitric oxide from such a view point.[4) Recently, Vaska and Nakai[5) reported a peculiar addition reaction of nitric oxide to chlorotetraphenylporphinato iron(III)[FeClTPP]. We have preliminary results that simple porphyrins catalytically reduce nitric oxide with molecular hydrogen at elevated temperatures.

The complexes examined in this work were cobalt-tetraphenylporphine(Co-TPP) and copper-tetraphenylporphine(Cu-TPP) which were prepared according to the literature.[6) The supported catalyst was prepared by impregnation of silica-alumina(13% Al_2O_3) in benzene solution of metal-TPP. The catalytic reduction of nitric oxide was observed by means of a usual flow reactor with a fixed catalyst bed. The amount of catalyst used, the partial pressure of nitric oxide, and the flow rate of hydrogen as a carrier gas were 0.45g, 0.03atm, and 60ml/min, respectively.

The catalytic activities of Co-TPP and Cu-TPP at several reaction temperatures are shown in Tables 1 and 2, respectively. The products of the reduction were nitrogen, ammonia, and nitrous oxide, of which portions are summarized also in Tables 1 and 2. The catalytic activities of the porphyrins were not so high as those of phthalocyanines.[4) The higher activity of cobalt is common to the case of phthalocyanine. The activity of the complex may have a relation with its oxidation potential. In the case of phthalocyanines, the activity for the reduction of NO formed a volcano shape pattern with a peak at Co-Pc against the oxidation potential of the complex,7) whereas their activity was reported to decrease monotonously with the increase of the oxidation potential for the dehydrogenation of cyclohexadiene.2)

The main products with Co-TPP were molecular nitrogen and ammonia, and their ratio did not change so much with the reaction temperature. In contrast, ammonia was the main product with Cu-TPP regardless of the reaction temperature. These results are also similar to the cases of phthalocyanines, although the product distributions with phthalocyanines changed with the reaction temperature.4) Further mechanistic study is now in progress.

The decomposition of the catalyst at the reaction conditions to affect the product distribution was ruled out because the activity continued for more than 4 days, and the amount of nitrogen in the products is much more than that in the catalyst used for the reaction. The color, IR, and X-ray diffraction pattern of the complexes did not change before and after the reaction, indicating that the major part of the catalyst maintained its structure during the reaction.

The complexes coagulated to form large particles after the reaction at the elevated reaction temperature, retarding the gas flow. To solve this problem, the complexes were dispersed on silica-alumina and their activities were observed. The results are shown in Table 3. The catalytic activity per unit weight of the TPP complex was much larger than that of unsupported one. Furthermore, no coagulation took place. The activity could be maintained for more than 2 days. No change of the product distribution may indicate that the silica-alumina enlarged the effective

Table 1. Catalytic Activity of Co-TPP for the Reduction of Nitric Oxide

Reaction temp.		280	310	340	370
NO conversion(%)		14	21	53	83
Yield(%)	N_2	6 (43)	8 (38)	28 (53)	49 (59)
	N_2O	1 (7)	2 (10)	4 (8)	6 (7)
	NH_3	7 (50)	11 (52)	21 (39)	28 (34)

Numbers in parentheses represent selectivities.
Partial pressure of nitric oxide : 0.03 atm
Catalyst:0.45g, Flow rate : 60 ml/min

Table 2. Catalytic Activity of Cu-TPP for the Reduction of Nitric Oxide

Reaction temp.		250	310	340	370
NO conversion(%)		9	20	32	35
Yield(%)	N_2	- (0)	2 (10)	8 (25)	6 (9)
	N_2O	- (0)	0.9 (4)	0.8 (3)	- (0)
	NH_3	9 (100)	17.1 (86)	23.2 (72)	29 (91)

Numbers in parentheses represent selectivities.
Partial pressure of nitric oxide : 0.03 atm
Catalyst:0.45g, Flow rate : 60 ml/min

Table 3. Catalytic Activities of supported Co-TPP and Cu-TPP for the Reduction of Nitric Oxide

Catalyst		Co-TPP-HA[a)]	Cu-TPP-HA[a)]
NO conversion(%)		74	22
Yield(%)	N_2	35 (47)	6.5 (30)
	N_2O	6 (8)	1.5 (7)
	NH_3	33 (45)	14 (63)
Increased Activity[b)] /unit weight of Me-TPP (times)		18.7	5.9

Numbers in parentheses represent selectivities.
Partial pressure of nitric oxide : 0.03 atm
Catalyst:0.93g, Flow rate : 60 ml/min
Reaction temp.:310°C

a) Silica-alumina (25% Al_2O_3)

b) The catalyst contains 9.1% Metal-tetraphenylporphine surface areas of metal-TPP, and kept it off from coagulation. A suitable supporter which can activate the catalyst through an electronic interaction may promise an excellent catalyst.

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